A USER'S GUIDE TO IPX, THE IN-PLACE POLLUTANT EXPORT WATER QUALITY MODELING FRAMEWORK

VERSION 2.7.4

Mark Velleux
Stephen Westenbroek
James Ruppel
Wisconsin Department of Natural Resources
Madison, Wisconsin 53701

Michael Settles[1]
OAO Corporation

Douglas Endicott[1]
U.S. Environmental Protection Agency

[1]Large Lakes Research Station
Grosse Ile, Michigan 48138

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U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
NATIONAL HEALTH AND ENVIRONMENTAL EFFECTS RESEARCH LABORATORY
MID-CONTINENT ECOLOGY DIVISION
LARGE LAKES RESEARCH STATION
GROSSE ILE, MICHIGAN 48138

DISCLAIMER

Development of the IPX framework was funded wholly or in part by the United States Environmental Protection Agency (USEPA). It has been subjected to the Agency's peer and administrative review, and has been approved for publication as an USEPA document. Mention of trade names, commercial products, or services, does not convey, and should not be interpreted as conveying, official USEPA approval, endorsement, or recommendation.

FOREWORD

The need to consider the environmental benefits and consequences of various management options continues to intensify as (1) environmental problems become more complex, (2) the means necessary to solve problems become more technical, time-consuming, and expensive, and (3) the costs to implement remedial strategies increase. Decisions which include remediation must be weighed carefully against the costs and effectiveness of the solutions. One environmental problem receiving considerable attention is that of contaminated sediments. The primary question is whether contaminated sediments should be remediated or left in place. Contaminated sediments are typically a legacy issue; however, continuing loads from other point and non-point sources confound clear solutions. Given the reality of limited funds for clean-up, environmental managers need to define what degree of remediation would achieve desired results and which sites are the priorities. In this regard, managers must justify expenditures and need to understand the environmental improvements expected to result from any remedial action on both local and lake-wide scales.

Mathematical models of environmental processes and effects offer an approach to help answer these questions and guide decisions on management options. These models should incorporate appropriate physical, chemical, and biological processes, as well as inputs of solids and chemicals. Model results must be confirmed using field-collected data for reliability and scientific credibility. Once the models are confirmed, the predictive capabilities for forecasting the degree of remediation, the environmental benefits, and the time necessary to realize those benefits can be used in the decision-making process. The IPX framework is one such tool and was specifically designed to address the transport and fate of in-place sediment pollutants.

IPX was initially developed during a comprehensive analysis of the Lower Fox River as part of the Lower Fox River/Green Bay Mass Balance Project and was used to predict future loadings to Green Bay under alternative remedial actions. Subsequently, IPX was successfully applied to the Buffalo and Oswego Rivers in New York. This document describes revisions and updates to IPX which have occurred during the Lake Michigan Mass Balance Study through application to rivers in the State of Wisconsin. Sufficient detail has been provided to allow other investigators to apply the IPX framework to other sites.

Development and application of complex, dynamic models should be approached with care, and requires the cooperation of a team of experts for any modeling endeavor. As is the case with the IPX framework, cross-agency effort and coordination has been required for many years; involving aspects such as sample collection, analyses, and database development; and including federal, state, and private sector efforts. It is recommended that users be familiar with basic water quality modeling techniques and associated theory regarding the transport and fate of chemicals in the aquatic environment. Finally, model development should be conducted in concert with monitoring and experimental research to provide data, estimates of model process rates, and in turn, reduce model uncertainties.

This report represents a collaborative effort among scientists and engineers at the USEPA, ORD, Mid-Continent Ecology Division, Large Lakes and Rivers Forecasting Research Branch and the Wisconsin Department of Natural Resources (WDNR). It is our desire that these efforts contribute to a more complete understanding of our environment and lead the way to practical improvements that enhance environmental quality.

AUTHORSHIP AND ACKNOWLEDGMENTS

Version 2.7.4 of the IPX Water Quality Modeling Framework was the result of a collaborative effort between the USEPA Large Lakes Research Station (LLRS) and the WDNR. The principal contributors were: Mark Velleux (WDNR), Stephen Westenbroek (WDNR), James Ruppel (WDNR), Michael Settles (OAO Corporation), and Douglas Endicott[1] (USEPA). Additional contributions in support of source code debugging were made by Michael Riley (S. S. Papadopulos and Associates). The version number of this release (Version 2.7.4) corresponds to the revision level assigned to the source code with the Revision Control System (RCS) for file management.

IPX Version 2.7.4 User's Guide

The IPX Version 2.7.4 user's guide was prepared by M. Velleux. This document was directly derived from the IPX (Version 1.0) user's guide (Velleux et al. 1994b). Portions of the document were adapted in whole or in part from the WASP4 User's Guide (Ambrose et al. 1988), the WASP5 User's Guide (Ambrose et al. 1993), and other documentation prepared during prior stages of IPX framework development. While it was not always possible to determine complete authorship for each element of the documentation, every effort has been made to appropriately credit the source authors for their contributions.

Chapter 1. IPX Model Theory: this chapter was adapted, in part, from the WASP4/WASP5 User's Guide. The source authors of the text from the user's guides were Robert B. Ambrose (USEPA), Tim Wool (Computer Sciences Corporation), John P. Connolly (Manhattan College), Robert W. Schanz (Woodward-Clyde Consultants), and James Martin (AScI Corporation). Text describing the settling and resuspension processes, photolysis, and volatilization was developed by M. Velleux, J. Gailani, and D. Endicott. Additional text describing the probability of deposition was summarized from QEA (1999). Text describing the semi-Lagrangian frame of reference for the sediment bed was developed by M. Velleux.

Chapter 2. IPX Input Data File Structure: this chapter was also adapted from the WASP4/WASP5 User's Guide. The source authors for much of this text were R. Ambrose, T.

[1] Present affiliation: Great Lakes Environmental Center, 739 Hastings Road, Traverse City, Michigan 49686.

Wool, J. Connolly, and R. Schanz, and J. Martin. Additional source authors were Kirk Freeman (Computer Sciences Corporation), D. Endicott, M. Velleux, and J. Gailani.

Chapter 3. IPX Output and Post-Processing. The source authors of this text were M. Velleux and K. Freeman.

Chapter 4. IPX Input Data File Pre-Processing. The source authors of this text were J. Gailani and M. Velleux.

Chapter 5. IPX Programmer's Guide. Significant portions of this chapter were adapted from the WASP4/WASP5 User's Guide with additional text and editorial modifications by M. Velleux. Text describing UNIX environment development tools for IPX was prepared by M. Settles.

The foreword to this report was prepared by Russell Kreis (USEPA) based on text written by William Richardson (USEPA). The preface was adapted from the WASP4/WASP5 User's Guide with text and editorial modifications by M. Velleux.

IPX Framework

In addition to the documentation effort, many people also contributed to source code development and programming efforts for the IPX framework. IPX Version 2.7.4 is an outgrowth of WDNR and USEPA efforts in support of the USEPA Lake Michigan Mass Balance Study. This version was developed from the first release of the IPX framework (Velleux et al. 1994b) and was derived from the WASP family of water quality modeling frameworks. Source code management using RCS was implemented by M. Settles at the LLRS. Additional programming support was also provided by M. Settles and Xiangsheng Xia (Computer Sciences Corporation). Initial development of IPX Version 2.7.4 was performed by M. Velleux with the assistance of S. Westenbroek and J. Ruppel and with contributions of D. Endicott. M. Riley provided source code debugging support and contributed the concept for ghost element collapse. Final programming and code development for Version 2.7.4 was performed by M. Velleux.

As noted above, IPX was derived from the WASP4 water quality modeling framework, which was itself derived from earlier frameworks, such as WASP and TOXIWASP developed with support from USEPA. During the earliest stages of the IPX development effort, WASP4 was significantly revised by K. Freeman and D. Endicott. Subsequent programming was performed by M. Velleux, K. Freeman, and Frank Mitchell (Computer Sciences Corporation).

Final programming and code development was performed by Keqin Shen (Computer Sciences Corporation), M. Velleux, J. Gailani, and D. Endicott.

Post-Processing Program

The W4DIS post-processing program was written by K. Freeman. Programming for Version 2.7.4 (W4DIS274) was performed by M. Velleux.

Pre-Processing Programs

The REDUCE pre-processing program was written by F. Mitchell with modifications by M. Velleux. The SETTLE and RESUSPND pre-processing programs were written by Anne Dame (USEPA), M. Velleux, and J. Gailani. Additional programming was performed by S. Westenbroek. The TIMESTEP pre-processing program was written by A. Dame and M. Velleux.

Other Contributions and Acknowledgments

Beyond those contributions already noted, many other individuals also contributed to the early development of IPX from WASP4. In particular, J. Martin and T. Wool (AScI Corporation) were often consulted during the initial stages of WASP4 use and debugging efforts at LLRS. W. Richardson, during his tenure as Chief of the LLRS, was very supportive of all IPX framework development efforts at each stage of the process. Debra Caudill (Computer Sciences Corporation) provided word processing support. All figures in this manual were revised and prepared by Kay Morrison (OAO Corporation). Finally, the support of Russell Kreis (USEPA), present Chief of the LLRS, is gratefully acknowledged.

PREFACE

Numerous frameworks are available to simulate the transport and fate of toxic chemicals in surface waters. Water quality modeling frameworks can range in complexity from simple, steady-state analytical solutions that describe a single first-order decay process to detailed, time-variable numerical solutions that describe the physical, chemical, and biological transfer and transformation processes affecting a chemical. As an outgrowth and extension of previous water quality modeling frameworks such as WASP (Di Toro et al. 1981), WASP4 (Ambrose et al. 1988), TOXIWASP (Ambrose et al. 1983), and WASTOX (Connolly and Winfield, 1984), the IPX framework was specifically designed to address the transport and fate of in-place pollutants in rivers and streams while retaining the flexibility needed to analyze a variety of water quality problems.

This manual describes IPX and is divided into five main sections. The first section, IPX Model Theory, documents the equations and assumptions underlying the IPX framework and components. Some guidance on using the framework is offered, along with typical input data values, when appropriate. More general summaries of the equations and possible input data values are provided in the "Rates Manual" (Bowie et al. 1985), the "Screening Manual" (Mills et al. 1985), and the "Toxicant Rates Manual" (Schnoor et al. 1987) as well as other texts cited in the references.

The second section, IPX Input Data File Structure, documents the input data specifications necessary to run IPX. Each data group is described, with input names, formats, and definitions. Convenient tabular summaries of environmental parameters, chemicals constants, and kinetic time functions are also provided.

The third section, IPX Simulation Output and Post-Processing, documents the output files created by IPX during a simulation as well as the W4DIS274 post-processing program. Short descriptions of each file are presented. A description of the W4DIS274 post-processor and examples of its use are also presented.

The fourth section, IPX Input Data File Pre-Processing, documents the pre-processing programs that accompany IPX. The pre-processors include REDUCE, SETTLE, RESUSPND, and TIMESTEP. Short overviews detailing the use of these programs and the structure of their input data are provided.

The fifth section, IPX Programmer's Guide, documents the general structure of the IPX program source code. First, a general warning is presented suggesting that users verify code operation. Second is a short section that describes porting IPX to various computational platforms. Finally, descriptions of the major subroutines and their calling sequence, common blocks (including how to re-dimension IPX for custom applications), and input/output units are presented.

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CHAPTER 1

IPX MODEL THEORY

1.1 IPX FRAMEWORK OVERVIEW

IPX, the **I**n-place **P**ollutant e**X**port model, is a dynamic compartment (control volume) water quality modeling framework specifically designed to simulate the transport and fate of sediments and associated hydrophobic contaminants in tributaries. IPX includes process descriptions for sediment aging, decreased sediment resuspendability with increasing age, and resuspension of freshly deposited sediments as a function of water velocity (shear stress at the sediment-water interface). These processes are needed to realistically simulate contaminant transport and substantially improve the model framework for application to tributary systems subject to significant deposition and resuspension events (where the shear stress is a function of water velocity). IPX has been applied, in a number of case studies, for estimating contaminant export from tributaries with contaminated sediments to receiving waterbodies (Velleux and Endicott, 1994a; Velleux et al. 1995; Velleux et al. 1996).

IPX evolved from a project to simulate the transport of polychlorinated biphenyls (PCBs) in the Lower Fox River, Wisconsin, as part of the EPA Green Bay Mass Balance Study (Velleux and Endicott, 1994a). For that project, the WASP4 water quality modeling framework (Ambrose et al. 1988) was used. In the course of applying WASP4 to model transport in the Fox River, limitations were encountered which led to its modification and, eventually, its evolution into IPX. In addition to sediment transport enhancements, IPX expands the contaminant simulation capabilities of WASP4 to allow simultaneous simulation of an unlimited number of contaminants (constrained only by available computer memory) while retaining most of the computation speed and flexibility of the original WASP4 framework. IPX may be considered a hybrid of WASP4, but because of significant changes in its capabilities and function, IPX is documented as an independent modeling framework. The publication by Velleux et al. (1996) provides further detail regarding the distinctions between IPX and WASP4.

The equations solved by IPX are based on the key principle of the conservation of mass. This principle requires that the mass of each water quality constituent (chemical or solid) simulated must be accounted for in one way or another. IPX traces each water quality constituent from each point of spatial and temporal input to all final points of export, thereby accounting for (conserving) mass in space and time. To perform these mass balance computations, the user must supply the framework with input data defining seven important characteristics:

- simulation and output control
- model segmentation
- advective, dispersive, and sediment transport
- boundary concentrations
- point and diffuse (non-point) source waste loads
- kinetic parameters, constants, and time functions
- initial concentrations

The input data define transport and transformation process parameters in the generalized mass balance equations that uniquely define the spatial and temporal domain of the water quality problem to be solved. These equations are numerically integrated using Euler's method. At user-specified print intervals, the values of all display variables are saved for subsequent retrieval by the W4DIS274 post-processor program. W4DIS274 allows the user to produce data tables of model output that can be subsequently graphed in any number of software packages. The output options available are discussed in Chapter 3.

1.2 THE GENERAL MASS BALANCE EQUATION

A mass balance equation for a water body accounts for all material entering and leaving the system by direct and diffuse loading, advective and dispersive transport, settling and resuspension, and physical, chemical, and biological transformations. Consider the coordinate system shown in Figure 1.1, where the x- and y-coordinates are in the horizontal plane, and the z-coordinate is in the vertical plane. The mass balance (partial differential) equation for an infinitesimally small fluid volume is:

$$\begin{aligned}\frac{\partial C}{\partial t} = &-\frac{\partial}{\partial x}\left(U_x C\right)-\frac{\partial}{\partial y}\left(U_y C\right)-\frac{\partial}{\partial z}\left(U_z C\right)\\ &+\frac{\partial}{\partial x}\left(E_x \frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(E_y \frac{\partial C}{\partial y}\right)+\frac{\partial}{\partial z}\left(E_z \frac{\partial C}{\partial z}\right)\\ &+S_L + S_B + S_K\end{aligned} \qquad (1.1)$$

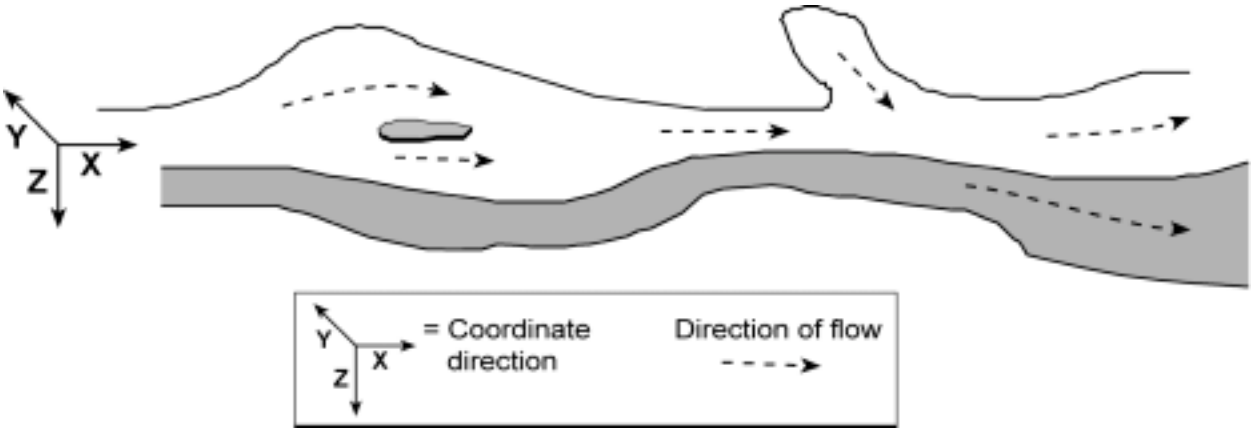


Figure 1.1. Coordinate system for mass balance equation.

where: C = concentration of the water quality constituent, mg/L (g/m^3) [M/L^3]
t = time, days [T]
U_x, U_y, U_z = longitudinal, lateral, and vertical advective velocities, m/day [L/T]
E_x, E_y, E_z = longitudinal, lateral, and vertical diffusion (dispersion) coefficients, m^2/day [L^2/T]
S_L = direct and diffuse loading rate, g/m^3-day [M/L^3/T]
S_B = boundary loading rate (including upstream, downstream, sediment, and atmospheric), g/m^3/day [M/L^3/T]
S_K = total kinetic transformation rate; positive indicates a source, negative a sink, g/m^3/day [M/L^3/T]

By expanding the infinitesimally small control volumes into larger adjoining "segments" and specifying transport, loading, and transformation parameters, a finite-difference form of Equation 1.1 is derived. The finite-difference form of the general mass balance equation is implemented in IPX. For brevity and clarity, however, the derivation of the finite-difference form of the mass balance equation is for a one-dimensional reach. Assuming vertical and lateral homogeneity, Equation 1.1 can be integrated over y and z to obtain:

$$\frac{\partial}{\partial t}(AC) = \frac{\partial}{\partial x}\left(-U_x AC + E_x A\frac{\partial c}{\partial x}\right) + A(S_L + S_B) + AS_K \qquad (1.2)$$

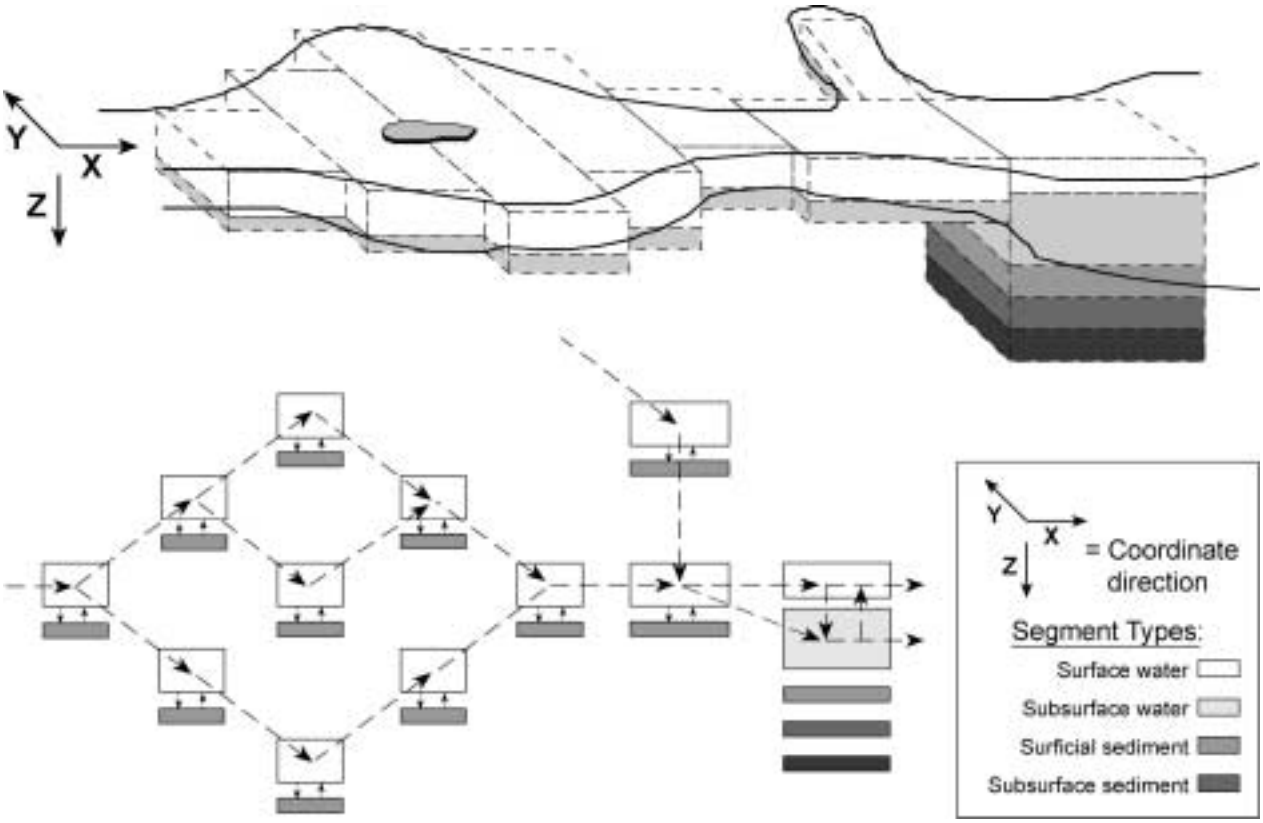


Figure 1.2. The model network: Model segmentation and segment types.

where: A = cross-sectional area, m^2 [L^2]

This equation represents the three major classes of water quality processes: transport (term 1), loading (term 2), and transformation (term 3). The finite-difference form of this equation is derived in Appendix A. The model network and the major processes are discussed in the following sections.

1.3 THE MODEL NETWORK/MODEL SEGMENTATION

The model network is a set of expanded control volumes or "segments" that together represent the physical configuration of the water body. As Figure 1.2. illustrates, the network may subdivide the water body laterally and vertically as well as longitudinally. The model

network can include sediment segments as well as water column segments. Concentrations of water quality constituents are calculated by solving the mass balance equation within each segment. Mass transport rates of each constituent are then calculated across the interface of adjoining segments.

Segments in IPX may be one of six types, as specified by the input variable ITYPE. A value of 1 indicates an epilimnion layer (surface water), 2 indicates a hypolimnion layer (subsurface water), 3 indicates a Eulerian surficial sediment layer, 4 indicates a Eulerian subsurface sediment layer; 5 indicates a semi-Lagrangian surface sediment layer, and 6 indicates a semi-Lagrangian subsurface sediment layer. The segment type is used to define aspects of sedimentation and transformation processes. The user must also specify the vertical organization of the model network. The segments immediately above and below each segment are specified by the input variables ITOPSG and IBOTSG. This alignment is important for determining mass transport due to burial and scour.

Segments are explicitly specified active compartments of the model network. During numerical integration of the mass balance equations, the model framework computes mass transport, transfer, and transformation terms for all active compartments. In addition to explicitly specified compartments, the semi-Lagrangian option for the sediment bed (Section 1.4.5.3) allows the user to also specify inactive compartments of the model network for the sediment bed. The network of inactive model segments is referred to as the "ghost" stack. Inactive compartments can enter or leave the active model network (thereby entering or leaving the ghost stack) in response to interactions within the sediment bed (decreases or increases of sediment bed elevation). With the semi-Lagrangian sediment bed option, it is also possible for the model to generate additional inactive compartments (beyond any initially specified) in response to interactions that increase sediment bed elevation. During numerical integration, the model framework does not perform mass balance computations on ghost stack elements.

In tributary models, segment volumes, river flows, and the simulation time-step are directly related. Segment volume and flow determine the hydraulic residence time (HRT). As HRT decreases, the simulation time-step must also decrease to insure stability and numerical accuracy. Segment size can vary dramatically, as illustrated in Figure 1.3. For any simulation, segment sizes may be dictated as much by the spatial and temporal scale of the simulation as by the physical characteristics of the system. For example, analyzing a simulation involving the upstream migration of a pollutant into a water supply near a river mouth due to flow reversals might require a time-step on the order of minutes. By contrast, analyzing a problem involving

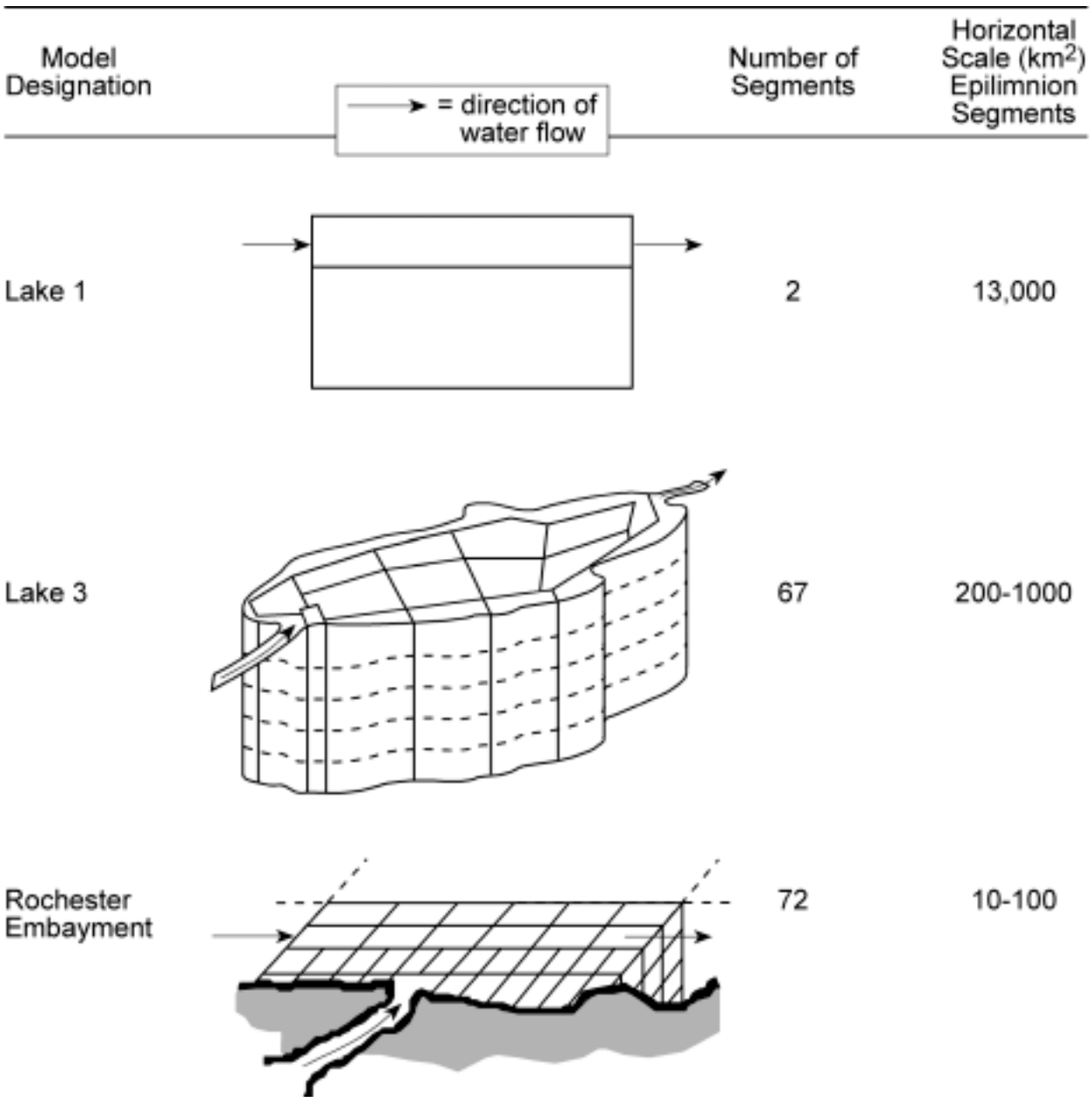


Figure 1.3. Spatial scales used for analysis of Lake Ontario.

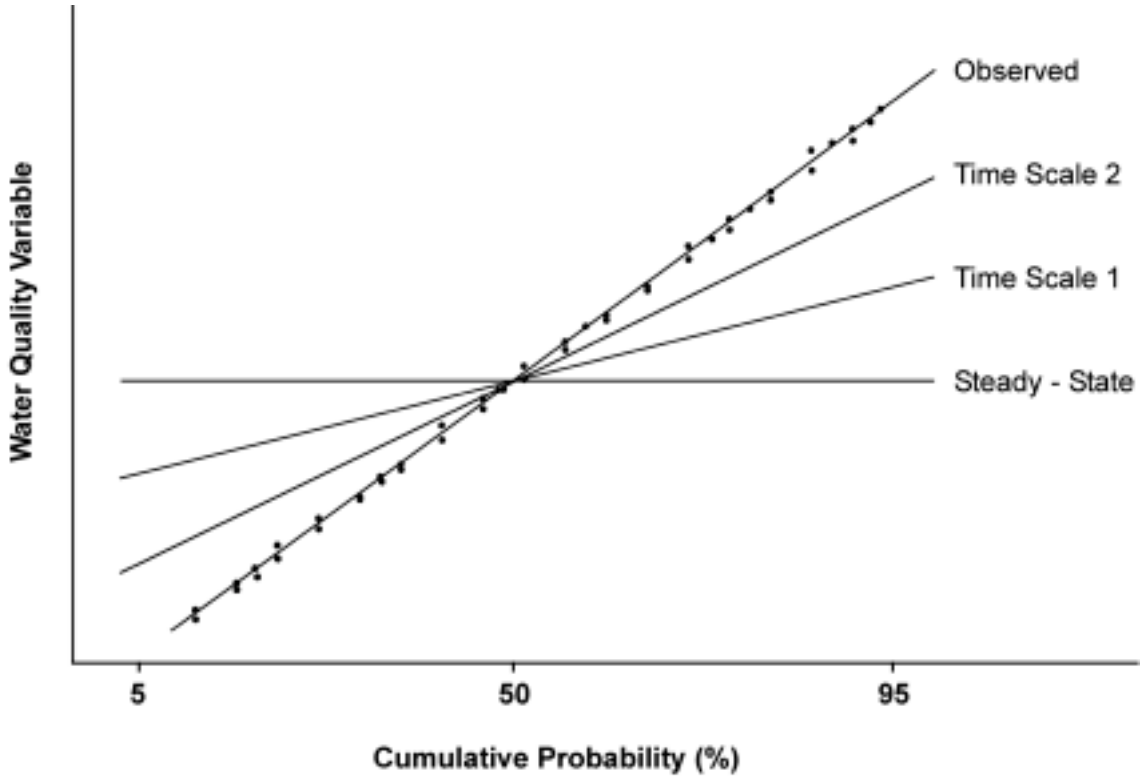


Figure 1.4. Example observed and calculated frequency distributions.

the total residence time of that pollutant in the same water body could allow a time-step of hours. As an example from a lake analysis consider the networks shown in Figure 1.3. The first network was used to study the general eutrophic status of Lake Ontario. The second network was used to investigate the lake-wide spatial and seasonal variations in eutrophication. The third network was used to predict changes in near-shore eutrophication of Rochester Embayment resulting from specific pollution control plans.

As part of the problem definition, the user must determine the accuracy to which the temporal and spatial variability of a contaminant's frequency distribution must be predicted. For example, a daily-average dissolved oxygen concentration of 5 mg/L would not sufficiently protect fish if fluctuations result in concentrations less than 2 mg/L for 10% of the time. However, predicting extreme concentration values is generally more difficult than predicting average values. Figure 1.4 illustrates typical frequency distributions predicted by three model

time scales and a typical distribution observed by rather thorough sampling as they would be plotted on probability paper. The straight lines imply normal distributions. While reducing model segment sizes (and consequently the model time-step) allows more accurate simulation of the frequency distribution, increased model accuracy requires increased temporal and spatial resolution of the model inputs such as loads and flow patterns.

When determining the temporal resolution of a simulation, care must be taken to preserve important non-linear interactions. When two or more important processes have different periods of variation, the temporal resolution of the simulation will generally be controlled by the time scale of the process with the greatest temporal variability. Temporal resolution may also be affected by the physical characteristics of the model system. For example, discontinuous batch discharges into a large lake might safely be averaged over a day or week, because large scale transport variations are relatively infrequent. However, it may not be possible to average the same batch discharge into a tidal estuary or river because of the semi-diurnal or diurnal tidal variations or seiche action. A third example is salinity intrusion in estuaries. Tidal variations in flow, volume, and dispersion can interact such that even long-term simulations may require model inputs and simulation time-steps on the order of hours. In general, the simulation time-step must be somewhat less than the temporal variability of the dominant mass transport/transfer pathways. For advectively dominated tributaries (where advective transport is the greatest mass transport pathway), a rough guide for determining the simulation time is to limit the time-step to one third the hydraulic residence time of the smallest water column segment in the model network.

Once the temporal variability has been determined, then the spatial variability of the water body must be considered. Generally, spatial characteristics must be homogeneous within a segment. In some cases, this restriction can be relaxed by judicious averaging over width, depth, and/or length. For example, depth governs the impact of reaeration and sediment oxygen demand in a column of water. Nevertheless, averaging the depth across a river is generally acceptable for conventional waste load allocation, whereas averaging the depth across a lake would not generally be acceptable. Other important spatial characteristics to consider (depending upon the problem being analyzed) include temperature, light penetration, velocity, pH, and the physical characteristics of the sediments, as well as sediment contaminant concentrations.

The expected spatial variability of the water quality concentrations also affects segment sizing. The user must determine to what extent averaging concentration gradients is acceptable. For example, water quality conditions change rapidly near a loading point but may stabilize

downstream. Studying the effects of the discharge on a beach one quarter mile downstream of a discharge point may require smaller segments than when studying the effects of the discharge on a beach several miles downstream.

A final, general guideline for obtaining accurate simulations is that water column segment volumes should be of roughly similar hydraulic retention times to minimize numerical dispersion. If river flows increase significantly downstream in the model network, then segment volumes should also increase proportionately. The user should define segment volumes for critical reaches of the system and then determine appropriate sizes for upstream and downstream segments accordingly.

The segment volumes specified must also be sized to best represent the actual spatial variability, as discussed above. Nonetheless, this guideline will allow use of larger time-steps and result in greater numerical accuracy over the entire model network, as explained in Section 1.11.

1.4 ADVECTIVE, DISPERSIVE, AND EVAPORATIVE TRANSPORT

Transport processes in IPX are divided into seven distinct types, or fields. Each field is associated with a data group of the model input file. Transport fields 1, 2, and 7 are used to specify advective, dispersive, and evaporative transport. Transport fields 3, 4, 5, and 6 are used to specify sediment transport. This section describes advective, dispersive, and evaporative transport and the operation of transport fields 1, 2, and 7. Sediment transport and the operation of transport fields 3, 4, 5, and 6 are described in Section 1.5.

The first transport field type moves all phases of each state variable (dissolved, bound, and particulate) and is used to specify advective flow and dispersive mixing in the water column. The second transport field moves only the dissolved and bound phases of each state variable and is used to specify the movement of pore water in the sediment bed. The seventh field moves water across the air-water interface (and can also be used to move state variables into but not out of the model) and is used to specify evaporation and precipitation.

1.4.1 Water Column Advection

Advective water column flows directly control the transport of dissolved and particulate pollutants in many water bodies. Advective flow moves water quality constituents downstream with the water and accounts for instream dilution. In addition, changes in velocity and depth which result from variable flows can affect such kinetic processes as reaeration, volatilization,

and photolysis. An important early step when developing a simulation is to properly describe water column advection. In IPX, water column flow is input via transport field 1 in Data Group D. As a user option, water column segment volumes are held constant or are allowed to vary in response to changes in flow as specified in Data Group C.

IPX tracks each separate inflow specified by the user from its point of origin and through each segment until it exits the model network. For each inflow, the user must supply a continuity or unit flow response function and a time function. The continuity function describes the spatial extent of the inflow response as it varies throughout the model network. The time function describes the temporal variability of the inflow. The actual flow between segments that results from a given inflow is the product of the time function and the continuity function. If several inflow functions are specified between any segment pair, then the total flow between segments is computed as the sum of the individual flow functions. In this manner, the effect of several tributaries joining, density currents, and wind-induced flow patterns can be described in a simple manner. For flow option 1 (IQOPT = 1), IPX sums all the flows within a segment to determine the direction of net flow and moves mass only in the direction of the net flow (one direction only). For flow option 2 (IQOPT = 2) IPX moves mass independently of net flow (more than one direction) to give the effect of large circulation patterns.

A good description of segment geometry as a function of flow conditions can be important when using IPX to simulate rivers. For flow option 1, a set of user-specified hydraulic discharge coefficients from Data Group C defines the relationship between velocity, depth, and stream flow. This method, described below, follows the implementation in QUAL2E (Brown and Barnwell, 1987).

Discharge coefficients giving depth and velocity from stream flow are based on empirical observations of the velocity-depth-stream flow relationship (Leopold and Maddox, 1953). It is important to note that these coefficients are only important when calculating reaeration. The velocity calculations are not used in time travel. The equations relate velocity, channel width, and depth to streamflow through power functions:

$$\mathrm{v} = aQ^{b} \tag{1.3}$$

$$\mathrm{D} = cQ^{d} \tag{1.4}$$

$$B = eQ^{f} \tag{1.5}$$

where: v = average water velocity, m/s [L/T]
D = average depth, m [L]
B = average width, m [L]
Q = flow, m^3/s [L^3/T]
a, b, c, d, e, f = empirical coefficients

Given that area is a function of channel width (B) and depth (D):

$$A = DB \tag{1.6}$$

From continuity, it is clear that:

$$\begin{aligned} Q &= vA \\ &= vDB \\ &= \left(aQ^b\right)\left(cQ^d\right)\left(eQ^f\right) \\ &= \left(ace\right)Q^{(b+d+f)} \end{aligned}$$

Therefore, the following relationships hold:

$$ace = 1 \tag{1.7}$$

$$b + d + f = 1 \tag{1.8}$$

IPX only requires that the relationships for velocity (Equation 1.3) and depth (Equation 1.4) be specified; coefficients for channel width (Equation 1.5) are implicitly specified by Equations 1.7 and 1.8.

These options can be put into perspective by noting that, for a given specific channel cross-section, the coefficients (a, c, e) and exponents (b, d, f) can be derived from the Manning equation. For example, if a channel of rectangular cross-section is assumed, then channel width (B) is not a function of streamflow (Q): the exponent (f) is zero (0.0) and the coefficient (e) is the width of the rectangular channel (B). By noting that hydraulic radius (R) is approximately equal to depth (D) for wide streams and that A = D B, the discharge coefficients for rectangular cross sections can be shown to be 0.4 for velocity and 0.6 for width.

Leopold et al. (1964) noted that stream channels in humid regions tend towards a rectangular cross-section because cohesive soils promote steep side slopes whereas non-cohesive

Table 1.1. Comparison of hydraulic exponents.

Channel Cross-Section	Exponent for Velocity (b)	Exponent for Depth (d)	Exponent for Width (f)
Rectangular	0.40	0.60	0.00
Average of 158 U.S. Gaging Stations	0.43	0.45	0.12
Average of 10 Gaging Stations on Rhine River	0.43	0.41	0.13
Ephemeral Streams in Semiarid U.S.	0.34	0.36	0.29

soils encourage shallow sloped, almost undefined banks. Table 1.1 compares hydraulic exponents for a rectangular channel with data reported by Leopold et al. (1964). Note that the average velocity exponent is relatively constant for all channel cross sections. The major variation occurs as a decrease in the depth exponent and concomitant increase in the width exponent as channel cross-sections change from the steep side slopes characteristic of cohesive soils to the shallow slopes of arid regions with non-cohesive soils.

For water bodies such as lakes and reservoirs, velocity and depth may not be functions of flow. For these cases, the velocity and depth exponents (b and d) can be chosen to be zero (0.0). Because Q to the zero power equals one (1.0), the coefficients a and c must be the velocity and depth: if b = 0, then a = V; if d = 0, then c = D. When the depth exponent is zero, IPX adjusts segment depth as a function of segment volume, assuming rectangular sides.

For site-specific river or stream simulations, hydraulic coefficients and exponents must be estimated. Brown and Barnwell (1987) recommended estimating the exponents (b and d) and then calibrating the coefficients (a and c) to observed velocity and depth. The exponents may be chosen based on observations of channel shape noted in a reconnaissance survey. If cross sections are largely rectangular with vertical banks, the first set of exponents shown in Table 1.1 should be useful. If channels have steep banks typical of areas with cohesive soils, then the second set of exponents is appropriate. If the stream is in an arid region with typically non-cohesive soils and shallow sloping banks, then the last set of exponents is recommended.

A key property of the channel that should be noted in a reconnaissance survey is the condition of the bank slopes or the extent to which width may expand with increasing

streamflow. Clearly the bank slopes and material in contact with the streamflow at the flow-rate(s) of interest are the main characteristics to note in a reconnaissance. Table 1.1 gives general guidance but it should be noted that values are derived for bank-full flows. Even in streams with vertical banks, the low flows may be in contact with a sand bed having shallow sloped, almost nonexistent banks more representative of ephemeral streams in semi-arid areas.

1.4.2 Water Column Dispersion

Dispersive water column exchanges significantly influence the transport of dissolved and particulate pollutants in such water bodies as lakes, reservoirs, and estuaries. Dispersion causes mixing and dilution between regions of high concentrations and regions of low concentrations. Even in advectively dominated systems such as rivers, longitudinal dispersion can be the most important process in diluting peak concentrations that may result from dynamic (unsteady) loads or spills. Natural or artificial tracers such as dyes, salinity, conductivity, or heat (temperature) are often used to calibrate dispersion coefficients for a model network.

In IPX, water column dispersion is input via transport field 1 of Data Group B. Any number of groups of exchanges may be defined by the user. For each group, the user must supply a time function giving dispersion coefficient values (in m^2/s) as they vary in time. For each exchange in the group, the user must supply an interfacial area, a characteristic mixing length, and the segments between which the exchange takes place. The characteristic mixing length is typically the distance between segment midpoints. The interfacial area is the area normal to the characteristic mixing length shared by the exchanging segments (cross-sectional area for horizontal exchanges, or surface area for vertical exchanges). The dispersive exchange between segments i and j at time t is given by:

$$\frac{\partial M_i}{\partial t} = \frac{E_{ij} A_{ij}}{L_{cij}} \left(C_j - C_i \right) \tag{1.9}$$

where: M_i = mass of chemical in segment i, g [M]

C_i, C_j = total chemical concentration in segments i and j, mg/L (g/m^3) [M/L^3]

$E_{ij}(t)$ = dispersion coefficient time function for exchange "ij", m^2/day [L^2/T]

Aij = interfacial area shared by segments i and j, m2 [L^2]

L_{cij} = characteristic mixing length between segments i and j, m [L]

1.4.3 Pore Water Advection

Pore water flows into or out of the sediment bed can significantly influence sediment pollutant concentrations. Dissolved or bound water quality constituents are carried through the

sediment bed by pore water flow. Depending on the direction of these flows, and the source of the pollutants, pore water advection may be a source or sink of pollutants to overlying waters.

If sediment segments are included in the model network, the user may specify advective transport of dissolved chemicals in the pore water. In IPX, pore water flows are input via transport field 2. Pore water advection transports water and dissolved chemical; sediment and particulate chemical are not transported. The mass derivative of chemical due to pore water flow from segment j to segment i is given by:

$$\frac{\partial M_i}{\partial t} = \frac{Q_{ij} f_{dj}}{n_j} C_j \qquad (1.10)$$

where: M_i = mass of chemical in segment i, g [M]
C_j = total chemical concentration in segment j, mg/L (g/m3) [M/L^3]
n_j = porosity of segment j, L_w/L (volume of water/volume total solution) [dimensionless]
f_{dj} = dissolved fraction of chemical in segments i and j [dimensionless]
Q_{ij} = pore water flow-rate from j to i, m^3/day [L^3/T]

The dissolved fraction of a contaminant (f_d) may be input by the user in Data Group J or computed from sorption kinetics.

IPX tracks each separate pore water inflow through the network of sediment segments. For each inflow (or outflow), the user must supply a continuity function and a time function. The actual flow through the sediment segments that results from each inflow is the product of the time function and the continuity function. If a flow originates in or empties into a surface water segment, then a corresponding surface water flow function must be described in flow field 1 that matches the pore water function.

1.4.4 Pore Water Diffusion

Diffusive exchanges between pore waters and with the overlying water column can significantly influence sediment pollutant concentrations, particularly for relatively soluble chemicals and water bodies with little sediment loading. Dissolved and bound water quality constituents can be exchanged between the sediment bed and the water column by pore water diffusion. Depending on the dissolved chemical concentration gradient, pore water diffusion may be a source or sink of pollutants to overlying waters.

If sediment segments are included in the model network, the user may specify diffusive transport of dissolved chemicals in the pore water. In IPX, pore water diffusion is input via transport field 2 in Data Group B. Any number of groups of exchanges may be defined by the user. For each group, the user must supply a time function giving dispersion coefficient values (in m^2/s) as they vary in time. For each exchange in the group, the user must supply an interfacial area, a characteristic mixing length, and the segments between which exchange takes place. For pore water diffusion between two sediment segments, the characteristic mixing length is typically the distance between two sediment segment midpoints; this length is multiplied by a tortuosity factor, which is internally computed in the framework as the inverse of porosity. For pore water exchange with a water column segment, the characteristic mixing length is usually taken to be the depth of the surficial sediment segment. The interfacial area is the surficial area of the sediment segment and is internally multiplied in the framework internally by the sediment porosity. The concentration of chemical diffusing is the dissolved fraction per unit volume of pore water. The actual diffusive exchange between sediment segments i and j at time t is given by:

$$\frac{\partial M_i}{\partial t} = \frac{E_{ij}(t) A_{ij}}{L_{cij}} \left(\frac{f_{dj} C_j}{n_j} - \frac{f_{di} C_i}{n_i} \right) \tag{1.11}$$

where: f_{di}, f_{dj} = dissolved fraction of chemical in i and j [dimensionless]
n_{ij} = average porosity at interface "ij", L_w/L (volume of water/volume total solution) [dimensionless]
$E_{ij}(t)$ = diffusion coefficient time function for exchange "ij", m^2/day [L^2/T]
A_{ij} = interfacial area shared by segments i and j, m^2 [L^2]
L_{cij} = characteristic mixing length between segments i and j, m [L]

1.4.5 Evaporation and Precipitation

Evaporation and precipitation can play a significant role in the overall water balance for some water bodies. These processes can also affect contaminant concentrations. Precipitation may be a low level source of some pollutants. As water evaporates, pollutant concentrations may increase. In IPX, evaporation and precipitation are input via transport field 7 of Data Group D. Different groups of segments having the same evaporation or precipitation rates may be defined by the user. For each group, the user must supply a time function giving evaporation or precipitation velocities (in m/sec). For each segment in the group, the user must also supply the surface area (in m^2) and a segment number pair. For evaporation the pair is from "ISEG" to "0" and for precipitation the pair is from "0" to "ISEG", where ISEG must be the number of a surface water segment. The precipitation input to segment i (i = ISEG) at time t is given by:

$$\frac{\partial M_i}{\partial t} = P_i(t) A_i C_{oi}(t) \tag{1.12}$$

where: $P_i(t)$ = precipitation velocity time function for segment i, m/day [L/T]
A_i = surface area of segment i, m^2 [L^2]
$C_{oi}(t)$ = concentration of pollutant in precipitation, mg/L [M/L^3]

In addition, segment volumes are adjusted:

$$\frac{\partial V_i}{\partial t} = A_i \left(P_i(t) - E_i(t) \right) \tag{1.13}$$

where: Ei(t) = evaporation velocity time function for segment i, m/day [L/T]

Although it is possible to simulate contaminant inputs to a water body by precipitation, there are limitations to this approach. IPX only allows the user to specify a single boundary condition for any given model segment. For example, consider a simple model network that is a single water column segment. This segment could have boundaries with surrounding water and sediments as well as with the atmosphere. However, the user can only input a single boundary condition for this segment and this one boundary condition will be applied to all transport processes across all boundaries. If contaminant concentrations at each boundary significantly differ, the boundary load computed for any process may not accurately represent the contaminant mass input to the segment. Consequently, precipitation inputs to the model are best treated as point loads rather than boundary conditions (loads).

It should be noted that no chemical or solids mass is transported out of the model by evaporation. Volatilization (Section 1.6.7) is used to describe the movement (loss or gain) of chemical state variables across the air-water interface. Also note that concentration changes attributable to changes in water segment volumes are automatically computed.

1.5 SEDIMENT TRANSPORT AND THE SEDIMENT BED

As noted in Section 1.4, transport processes in IPX are divided into seven distinct types, or fields. Transport fields 1, 2, and 7 are used to specify advective, dispersive, and evaporative transport. Transport fields 3, 4, 5, and 6 are used to specify sediment transport. This section describes sediment transport and the operation of transport fields 3, 4, 5, and 6. Advective,

dispersive and evaportative transport and the operation of transport fields 1, 2, and 7 are described in Section 1.4.

The third, fourth, and fifth transport field types move particles and particulate phase pollutants and are used to specify settling for each of three possible solids state variables that can be simulated. Transport field 3 moves particle state variable 1 and all chemical state variables associated with particle state variable 1. Similarly, transport field 4 moves particle state variable 2 and field 5 moves particle state variable 3, as well as all chemical state variables associated with those particles. The sixth transport field type moves particles and particulate phase pollutants and is used to specify resuspension for all possible particle state variables that can be simulated.

Note that transport fields 3-6 describe interactions between the water column and sediment bed. Interactions within the sediment bed, described by burial and scour (unburial), are automatically computed from the difference between the gross settling and resuspension fluxes. Two options are available to represent interactions within the sediment bed: 1) Eulerian, and 2) semi-Lagrangian. These options are described in Sections 1.5.3 and 1.5.4. Using either option, the user must specify the particulate fraction or partitioning parameters for each chemical. Initial (at t = 0) dissolved chemical fractions are entered in Data Group J.

1.5.1 Settling

Particles (sediments) and particulate phase chemicals in the water column may settle through water segments and deposit onto surficial sediment bed segments. Settling rates in IPX are described by velocities and surface areas in transport fields 3, 4, and 5 of Data Group D. Particle settling velocities may vary both in time and in space, and are multiplied by cross-sectional areas to obtain transport rates for solids and the particulate fractions of chemicals.

An upper bound for particle settling velocities is given by Stokes' Law:

$$v_s = \frac{8.64g}{18\mu}(\rho_p - \rho_w)d_p^2 \qquad (1.14)$$

where: v_s = Stokes' velocity for a particle of diameter d_p and density ρ_p, m/day [L/T]
g = acceleration of gravity = 981 cm/sec^2 [L/T^2]
μ = absolute viscosity of water = 0.01 poise (g/cm-sec) at 20°C [M/L/T]
ρ_p = density of particle, g/cm^3 [M/L^3]
ρ_w = density of water, g/cm^3 [M/L^3]

Table 1.2. Stokes' settling velocities for a range of particle sizes and densities at 20°C.

Particle Diameter, mm	Particle Density, g/cm^3			
	1.80	2.00	2.50	2.70
	Stokes' Law Settling Velocity (m/day)			
Fine Sand				
0.3	300	400	710	800
0.05	94.0	120	180	200
Silt				
0.05	94.0	120	180	200
0.02	15.0	19.0	28.0	32.0
0.01	3.80	4.70	7.10	8.00
0.005	0.94	1.20	1.80	2.00
0.002	0.15	0.19	0.28	0.32
Clay				
0.002	0.15	0.19	0.28	0.32
0.001	0.04	0.05	0.07	0.08

d_p = particle diameter, mm [L]

Stokes' Law settling velocities for a range of particle sizes and densities are presented in Table 1.2.

While Stokes' Law is a valid means to approximate the settling velocity of discrete, spherical particles under quiescent conditions, the actual rate at which particles settle is often substantially less than predicted by Equation 1.14. In addition, sediment particle sizes, and therefore settling velocities, typically vary over several orders of magnitude (Lee et al. 1981; Filkins et al. 1993). As a result, it is difficult to estimate settling velocities without detailed consideration of the characteristics of the particles to be simulated. To accommodate this range of characteristics, it is useful to divide the range of suspended solids into three particle classes: coarse, medium, and fine. These classifications divide the particle grain size distribution into more easily defined groups whose properties are less difficult to characterize.

Coarse particles (>62 μm) are generally non-cohesive and, compared to finer particles, may settle at rates similar to those described by Stokes' Law under quiescent conditions. However, since natural particles are rarely spherical Stokes' Law may overestimate settling velocities. A number of empirical relationships describing settling velocities of non-cohesive

particles such as sands are available. A summary of representative relationships is presented by Yang (1996). For non-cohesive (fine sand) particles with diameters from 62 to 500 μm, settling velocity can be computed as (Cheng, 1997):

$$v_s = \frac{\nu}{d_p}\left[\left(25 + 1.2 d_*^2\right)^{0.5} - 5\right]^{-1.5} \tag{1.15}$$

$$d_* = d_p\left[\frac{(S-1)g}{\nu^2}\right]^{1/3} \tag{1.16}$$

where: v_s = quiescent settling velocity, m/s [L/T]
ν = kinematic viscosity of water, m^2/s [L^2/T] = 1.007×10^{-6} at 20 °C
d_p = average particle diameter, m [L]
d_* = non-dimensional particle diameter [dimensionless]
S = specific gravity of particle [dimensionless] = 2.65 for pure sands
g = gravitational acceleration, m/s^2 [L/T^2] = 9.81

Medium particles (<62 μm) are often cohesive and may flocculate. Floc size and settling speed depend on the conditions under which the floc was formed (Burban et al. 1990). Settling velocities of cohesive particles can be approximated by:

$$v_s = B_1\left(m_1 G\right)^{-0.85} d_m^{-[0.8+0.5\log(m_1 G - B_2)]} \tag{1.17}$$

$$G = C_d \rho\left(v_A\right)^2 \tag{1.18}$$

where: v_s = floc settling velocity cm/s [L/T]
B_1 = experimentally determined constant = 9.6×10^{-4}
G = internal fluid shear stress, $dynes/cm^2$ [$M/L/T^2$]
d_m = median floc diameter, cm [L]
B_2 = experimentally determined constant = 7.5×10^{-4}
C_d = coefficient of drag [dimensionless] = 0.0015 for internal fluid shear stress
v_A = advective velocity, cm/s [L/T]

Under conditions typically found in tributaries, floc settling speeds range from 60-160 μm/s (Burban et al. 1990).

Fine particles (<10 μm) generally may not extensively flocculate and typically have the smallest settling velocities as a result of their size, shape, density, and other physicochemical

properties. For example, clay particles often have negative electrical charges which can inhibit direct particle aggregation in dilute suspensions. Also, biotic materials such as algae often fall into this size class of particles. Algae in particular generally possess a variety of mechanisms to minimize their settling velocities (Wetzel, 1983). As a result of these attributes and other conditions, fine particles may have near-zero settling velocities. For simplicity, the settling velocity of fine particles is often represented by a small constant value.

Not all particles settling through the water column will necessarily reach the sediment-water interface or otherwise be incorporated into the sediment bed. As a result, effective settling velocities of particles in flowing water are usually less than quiescent settling velocities. The effective settling velocity can be described as a reduction in the quiescent settling velocity by the probability of deposition:

$$v_{se} = P_{dep} v_s \tag{1.19}$$

where: v_{se} = effective settling velocity [L/T]
P_{dep} = Probability of deposition [dimensionless]

The probability of deposition varies with shear stress near the sediment bed and particle size. As particle size decreases or shear stress increases, the probability of deposition decreases.

For non-cohesive particles, the probability of deposition has been described as a function of bottom shear stress (Gessler, 1967):

$$P_{dep} = P = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y} e^{-0.5x^2} dx \tag{1.20}$$

$$Y = \frac{1}{\sigma}\left(\frac{\tau_{cd,n}}{\tau} - 1 \right) \tag{1.21}$$

where: P = probability integral for the Gaussian distribution
σ = experimentally determined constant = 0.57
$\tau_{cd,n}$ = critical shear stress for deposition of non-cohesive particles, defined as the shear stress at which 50% of the particles in the size class settle

The critical shear stress for non-cohesive deposition, τ_{cd}, can be computed by determining the upward force needed to balance the net downward force (gravity force minus the sum of the

buoyant and drag forces) for a particle with a diameter equal to the mean diameter of the size class (i.e. $d_p = d_{50}$).

For cohesive particles, the probability of deposition has been described as a function of bottom shear stress (Patheniades, 1992):

$$P_{dep} = 1 - P = 1 - \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y} e^{-0.5x^2} dx \tag{1.22}$$

$$Y = \frac{1}{\sigma} \ln\left[0.25\left(\frac{\tau_{cd,c}}{\tau} - 1 \right) e^{1.27\tau_{cd}} \right] \tag{1.23}$$

where: σ = experimentally determined constant = 0.49
$\tau_{cd,c}$ = critical shear stress for deposition of cohesive particles, defined as the shear stress at which 100% of the particles in the size class settle

The probability integral in Equations 1.20 and 1.22 can be approximated as (Abramowitz and Stegun, 1972):

$$\begin{aligned} P &= 1 - F(Y)\left(0.4362X - 0.1202X^2 + 0.9373X^3\right) && \text{for } Y > 0 \\ P &= 1 - P(|Y|) && \text{for } Y < 0 \end{aligned} \tag{1.24}$$

$$F(Y) = \frac{1}{\sqrt{2\pi}} e^{-0.5Y^2} \tag{1.25}$$

$$X = (1 + 0.3327Y)^{-1} \tag{1.26}$$

It is not always necessary or desirable to have more than one state variable to represent solids. When explicit representation of multiple particle types is not desired, it is possible to conceptually represent multiple particle types as a single state variable by characterizing the particle grain size distribution as a function of flow as described by Gailani et al. (1991). Under low flow conditions, fine particles predominate with a small fraction of medium materials. At moderate flows, medium materials predominate with a smaller amount of fine particles and the potential for a minor fraction of coarse materials. At high flows, one of two conditions may exist: 1) on the rising limb of the hydrograph (at the beginning of a flow event) most suspended solids originating from the sediment bed will be medium particles until the flow peak is reached (when shear stresses at the sediment water interface are highest) and significant erosion of coarse

Table 1.3. Generalized grain size distribution functions for regulated tributaries.

Condition	River Flow	Fine (f_f)	Medium (f_m)	Coarse (f_c)	Eq.
Non-Event	$Q \le Q_{70}$	0.8	0.2	0.0	(1.27)
	$Q_{70} < Q \le Q_{80}$	0.0	1.0	0.0	(1.28)
Event: Rising Limb	$Q_{80} < Q \le Q_m$	$0.8 - \frac{3.2}{Q_{50}}(Q - Q_{70})$	$0.2 + \frac{3.2}{Q_{50}}(Q - Q_{70})$	0.0	(1.29)
Event: Falling Limb	$Q_{98} < Q \le Q_m$	0.0	0.3	0.7	(1.30)
	$Q_{80} < Q \le Q_{98}$	0.0	$0.3 + \frac{0.31}{Q_{50}}(Q - Q_{80})$	$0.7 - \frac{0.31}{Q_{50}}(Q - Q_{80})$	(1.31)

Table 1.4. Generalized grain size distribution functions for unregulated tributaries.

Condition	River Flow	Fine (f_f)	Medium (f_m)	Coarse (f_c)	Eq.
Non-Event	$Q \le Q_{99.9}$	0.6	0.4	0.0	(1.32)
Event: Rising Limb	$Q_{99.9} < Q \le Q_m$	0.03	0.2	0.5	(1.33)
Event: Falling Limb	$Q_{98} < Q \le Q_m$	0.3	0.2	0.5	(1.34)
	$Q_{80} < Q \le Q_{98}$	0.3	0.7 - 0.005Q	0.005Q	(1.35)

particles occurs; 2) on the falling limb of the hydrograph most sediments will initially be coarse. A general characterization of particle grain size distributions in both tributaries where flows are regulated and unregulated tributaries is expressed by the relationships presented in Tables 1.3 and 1.4. The variables used in Equations 1.27 through 1.35 are:

Q = river flow (m3/s) [L^3/T]

Q_{nn} = river flow at the nn percentile; nn = 50th, 70th, 80th, 98th, and 99.9th percentile (m^3/s) [L^3/T]

Q_m = the maximum river flow occurring during an individual event (m^3/s) [L^3/T].

It should be noted that these relationships are broad generalizations.

When simulating solids as a single state variable (TSS), overall particle settling rates are computed as a function of the particle size distribution and the settling velocities of each particle class:

$$v_s = f_c v_{sc} + f_m v_{sm} + f_f v_{sf} \quad (1.36)$$

where: v_s = total suspended solids (TSS) settling velocity [L/T]
v_{sc} = coarse particle class settling velocity [L/T]
v_{sm}= medium particle class settling velocity [L/T]
v_{sf} = fine particle class settling velocity [L/T].
f_c = fraction of coarse class particles
f_m = fraction of medium class particles
f_f = fraction of fine class particles

When simulating solids as two or three independent state variables, the particle grain size distribution functions can be used to divide total solids loads into loads for each state variable.

1.5.2 Resuspension, Sediment Aging, and the Surficial Sediments

Particles and particulate phase chemicals in the sediment bed may resuspend from the surficial sediments and return to the water column. Resuspension rates in IPX are described by velocities and surface areas in transport field 6 of Data Group D. Unlike settling, where the user must input settling velocities for each particle type state variable simulated, **only one transport field is used to specify resuspension velocities even if more than particle state variable is simulated**. IPX is designed so that all particle types simulated resuspend in proportion to their abundance. Particle resuspension velocities may vary both in time and in space, and are multiplied by cross-sectional areas to obtain transport rates for solids and the particulate fractions of chemicals.

Particles leaving the water column by settling enter the surficial layer of the sediment bed. IPX allows the user to define two sediment bed types on the basis of vertical location: surficial and subsurface sediments. Surficial sediments are comprised of age layers. Sediments settling to the bed over any defined interval (generally one day) enter the surficial age layer of surficial sediments. IPX allows the user to define an arbitrary number of sediment age layers. Sediments in each layer undergo an aging process characterized by changes in the physical characteristics of the layer. These changes alter the erosion potential of the sediment bed. Freshly deposited sediments are more resuspendable than those that have undergone some degree of aging. With respect to its impact on sediment erosion potentials, the sediment aging process is typically

completed in seven days (Tsai and Lick, 1987; Xu, 1991). Sediments in the final age layer of surficial sediment have the lowest resuspension potential. Not all age layers within surficial sediment segments will necessarily hold sediment at all times during a simulation. Frequently, the oldest layer will hold most of the sediment mass.

For any given resuspension event, the particle resuspension flux can be described as a function of the shear stress at the sediment-water interface, which can in turn be approximated as a function of flow (Ziegler et al. 1988; Gailani et al. 1991):

$$\varepsilon_{\tau>\tau_c} = \frac{a_0}{Z}\left(\frac{\tau-\tau_c}{\tau_c}\right)^m \qquad \text{for } \tau > \tau_c \tag{1.37}$$

$$\varepsilon_{\tau\le\tau_c} << \varepsilon_{\tau>\tau_c} \qquad \text{for } \tau \le \tau_c$$

$$\tau = C_f \rho (v_A)^2 \tag{1.38}$$

where: $\varepsilon_{\tau>\tau_c}$ = amount of sediment resuspended when the shear stress exerted at the sediment-water interface (τ) exceeds the critical shear for entrainment (τ_c), g/cm^2 [M/L^2]

a_0 = empirical sediment yield constant

Z = empirical sediment age constant

τ = shear stress exerted at the sediment-water interface, dynes/cm^2 [M/L/T^2]

τ_c = critical shear stress for entrainment, dynes/cm^2 [M/L/T^2]

m = empirical sediment entrainment exponent

$\varepsilon_{\tau\le\tau_c}$ = the amount of sediment resuspended when τ is less than or equal to the critical shear for entrainment, g/cm^2 [M/L^2]

C_f = coefficient of friction [dimensionless] = typically 0.002 - 0.004

v_A = advective water velocity, cm/sec [L/T]

The parameters τ_c, m, a_0, and Z depend on the physical characteristics (age, water content, cohesiveness, etc.) of a particular sediment. Once τ_c is exceeded, sediments are quickly entrained. From the amount resuspended (ε), a resuspension velocity can be computed:

$$v_r = \frac{\varepsilon}{\rho_b t_e} \tag{1.39}$$

where: v_r = resuspension velocity [L/T]

ρ_b = bulk density of sediments [M/L^3]

t_e = time to entrain sediments [T]

The most significant factor controlling erosion is the shear stress exerted at the sediment-water interface by water flowing over the sediments, τ. When τ exceeds the critical shear for entrainment, significant resuspension can occur. IPX dynamically computes τ for each surficial sediment segment as a function of the river flow and channel cross-sectional area as described in Equation 1.38.

When average shear stresses are below the critical value, resuspension may occur at a background level that is significantly less than when shear stresses exceed the critical threshold. This is defined as background resuspension. Background resuspension is a lumped parameter used to represent any particle movements that can occur when the average shear stresses are less than the average critical shear stress for erosion. Very fresh sediments can form "fluff" layers that have significantly different erosion properties (greater yields coefficients and much lower critical shear stresses) than older sediments (Gailani et al. 1991). In addition, bed sediments are comprised of a mixtures of particle types and sizes. Even within a single size class, particles smaller than the average particle size (d_{50}) may begin to resuspend before larger particles within the class. Background resuspension is typically so small that it does not significantly impact sediment bed morphometry or resultant suspended solids concentrations in the water column. However, in tributaries with significant in-place pollutant reservoirs, hydrophobic contaminants are typically present in the sediments at levels much higher than found in the water column relative to particulate materials. As a consequence, even minute resuspension (a little as several mm/year) can result in significant increases in water column contaminant concentrations. Therefore, although background resuspension is typically unimportant for accurate sediment transport simulation, it is necessary to accurately simulate contaminant transport.

Other significant factors that influence erosion are sediment armoring and the extent of sediment aging. These factors are described through the parameters τ_c, m, a_0, and Z. Sediments armor in response to the differential erosion of finer-grained, more easily resuspendable particles from the sediment bed, which leaves behind less resuspendable materials. IPX tracks the computed shear stress exposure history of the sediments. As a resuspension event progresses, the shear stress to which the sediments have been exposed increases (τ_c increases), armoring the sediment bed, and making further resuspension more difficult. IPX also automatically resuspends fresh, readily erodible sediments (with a low τ_c) that settle over an armored layer (with a high τ_c) during periods such as the declining limb of an event when the shear stress exerted at the sediment-water interface is less than the critical shear for resuspending the armored

sediments but is greater than the shear needed to resuspend fresh (unarmored, less consolidated) sediments ($\tau_{c_{fresh}} \leq \tau < \tau_{c_{armored}}$). The parameters a_0 and m express how readily erodible a given sediment is. Sediment resuspension is a highly nonlinear function of flow. Laboratory experiments have determined that for many sediments m is in the range of 2 to 3 (Xu, 1991; Lick et al. 1995). For a limited number of sediments, a_0 has been determined to be in the range of 0.27×10^{-3} to 8×10^{-3} (Xu, 1991, Lick et al. 1995). The parameter Z expresses the effect of sediment age on resuspension. Z is an exponential function of the time after deposition of the sediments in a given age layer and can vary from 0.1 to 50 (Tsai and Lick, 1987; Xu, 1991).

When computing resuspension velocities from Equations 1.37 - 1.39, the sediment age factor (Z) of the first age layer should be used for Equation 1.37. Z for the first age layer may differ from river reach to reach, however. In this manner, the resuspension potential of each age layer can vary relative to the resuspension potential of the first age layer as resuspension proceeds through each age layer. Users should also be aware that Equation 1.37 is applicable to cohesive sediments. However, sediments largely comprised of non-cohesive particles do not armor as extensively as cohesive sediments. As a consequence, during a resuspension event non-cohesive sediments will continue to resuspend (beyond the amount ε that would be applicable to cohesive sediments) until the shear stress at the sediment-water interface falls below the critical shear or the supply of resuspendable sediments is exhausted.

1.5.3 Burial and Scour (Unburial)

Burial and scour (unburial) are the sediment transport processes by which particles and contaminants interact within the sediment bed. Two options are available for representing these interactions: 1) Eulerian, and 2) semi-Lagrangian. The sediment bed option is determined by value of the input variable ITYPE (defined in Section 2.2.3). Sediment segments where ITYPE is 3 or 4 use an Eulerian frame of reference. With an Eulerian frame of reference, an open boundary exists at the bottom of the sediment stack. For each Eulerian sediment stack, the user specifies a boundary condition at the bottom of the stack and material can move into or out of the model network across the bottom boundary. Sediment segments where ITYPE is 5 or 6 use a semi-Lagrangian frame of reference. With a semi-Lagrangian frame of reference, a barrier (such as bedrock or hardpan materials) exists at the bottom of the sediment stack. For each semi-Lagrangian sediment stack, no boundary condition at the bottom of the stack is specified (since there is no open boundary) and no material moves into or out of the model network across the bottom barrier. For any stack of sediments (from the sediment-water interface to the bottom-most layer identified), consistent specification of the sediment column as Eulerian or semi-Lagrangian is necessary. For example, specification of a sediment stack with an Eulerian surface

layer (ITYPE = 3) and semi-Lagrangian subsurface layers (ITYPE = 6) directly below will cause a simulation error condition.

1.5.3.1 Eulerian Option

With the Eulerian sediment bed option, the model frame of reference is fixed at the sediment-water interface. Particles and associated contaminants move between surficial and subsurface sediment segments by burial and scour. Burial (which may be positive or negative in direction) is automatically computed in the framework from the difference between the particle settling and resuspension fluxes; the user does not specify burial/scour velocities.

The solids concentration in all sediment segments is held constant. The volume (depth) of all surficial sediment segments is allowed to vary from their initial values in response to erosion and deposition. The volume of all subsurface sediment segments is held constant. At a user defined interval, representative of the physical, biological, and chemical processes that change sediment properties, solids mass and associated contaminants are buried or scoured as needed to restore all surficial sediment segments to their initial volumes:

$$J_B = \Delta M = \Delta V C_2 = \sum_{i=1}^{n} \mathrm{v}_s(t_i) A C_1(t_i)(t_i - t_{i-1}) - \sum_{i=1}^{n} \mathrm{v}_r(t_i) A C_2(t_i)(t_i - t_{i-1}) \qquad (1.40)$$

where: J_B = burial flux, g [M]
ΔM = change in particle mass of the surficial sediment, g [M]
ΔV = change in volume of the surficial sediment segment, m^3 [L^3]
$t_i - t_{i-1}$ = time interval over which settling, resuspension occur, days [T]
v_s = settling velocity, m/day [L/T]
v_r = resuspension velocity, m/day [L/T]
C_1 = solids concentration in the water column, mg/L (g/m^3) [M/L^3]
C_2 = solids concentration in the surficial sediment, mg/L (g/m^3) [M/L^3]
A = interfacial area across which settling or resuspension occurs [L^2]

Whenever burial is computed, sediment (particle) mass is moved (advected) through all subsurface sediment segments that underlie a given surficial sediment segment (forming a vertical stack) as needed to restore the surficial sediment segment volume to its initial value. When burial is positive, sediment mass is moved from the surficial sediments, through the all subsurface sediments, and across the bottom boundary of the model while pore water and associated chemicals are “squeezed out” of each layer and transported to the layer above. When

burial is negative (scour), sediment mass is moved from the bottom boundary of the model, into the bottom segment, through the all subsurface sediments, and into the surficial sediments.

1.5.3.2 Semi-Lagrangian Option

With the semi-Lagrangian sediment bed option, the model frame of reference is fixed to the bottom of the sediment column (including any elements in the ghost stack) and the elevation of the sediment-water interface is allowed to float (relocate) in response to sediment transport. Particles and associated contaminants "move" between surficial and subsurface sediment segments and the ghost stack by a segment re-indexing procedure analogous to burial and scour. Segment re-indexing may be downward or upward in direction. The downward re-indexing of segments is referred to as "push" (analogous to burial) and the upward re-indexing as "pop" (analogous to scour). Segment re-indexing is automatically computed in the framework based on the surficial sediment segment volume (depth) conditions (which is itself determined by the difference between the particle settling and resuspension fluxes); the user does not specify burial/scour velocities.

The solids concentration in all sediment segments is held constant. The volume (depth) of all surficial sediment segments is allowed to vary from their initial values in response to erosion and deposition. The physical characteristics (including volume) of all subsurface sediment segments is held constant until a re-indexing event occurs. Re-indexing occurs when the surficial sediment segment reaches the minimum or maximum volume (depth) condition specified by the user. When a re-indexing event occurs, model sediment segments and ghost stack elements exchange identity to account for the net increase or decrease in sediment bed elevation. When segments exchange identity, the properties of each segment/ghost are assigned to a neighboring segment (or ghost stack element) below (push) or above (pop) throughout the sediment stack. In response to reaching the maximum volume condition, the surficial sediment segment is split to form two segments (one surficial and one subsurface) and all subsurface sediment segments (and ghost stack elements) are "moved" one element down the stack. When this occurs, the sediment stack at that location will contain one additional member and the total sediment bed elevation at that location increases. In response to reaching the minimum volume condition, the residual volume (if any) of the surficial sediment segment is joined with the subsurface segment (or ghost stack element) immediately below to form one surficial segment and all subsurface sediment segments (and ghost stack elements) are "moved" one element up the stack. When this occurs, the sediment stack at that location will contain one less member and the total sediment bed elevation at that location decreases. Note that after upward re-indexing,

the formerly occupied bottom-most segment or ghost will be "empty" (unoccupied). In this manner, mass is never transported out of or into the model network across the bottom barrier.

Sediment bed elevations at any location can change over time. In cases where the total supply of sediments in the sediment column at any location is exhausted, the volume of all segments (and ghost stack elements) can be zero. Zero sediment volume represents reaching the barrier at the bottom of the sediment column at that location. When this occurs, no further loss of sediments (i.e. resuspension) can occur, regardless of the resuspension velocity specified, because no sediments are available to resuspend. If sediments deposit to the barrier at the bottom of the sediment column, the sediment column is reconstructed (from the top down) once stack element at a time. In cases where sediment bed elevation increases beyond the initial elevation of the sediment column, elements are added to the ghost stack until all "empty" (unoccupied) elements in the stack are filled.

1.5.4 The Sediment Bed

The sediment bed plays an important role in the transport and fate of hydrophobic contaminants. Particles and associated pollutants in the surficial sediments may enter deeper sediment layers by burial or be returned to the surficial sediments by scour. The movement of particles and contaminants is automatically computed in IPX; the user does not specify burial velocities. Interactions between segments in the sediment column depend on specification of the Eulerian or semi-Lagrangian sediment bed options as presented in Section 1.5.3.

1.5.4.1 Surficial Sediments

As described in Section 1.5.2. the surficial sediments are comprised of age layers. IPX allows the user to define an arbitrary number of sediment age layers. Sediments settling to the bed over any defined interval (generally one day) enter the surficial age layer of surficial sediments. Sediments in each layer undergo an aging process characterized by changes in the physical characteristics of the layer. These changes alter the erosion potential of the sediment bed. Freshly deposited sediments are more resuspendable than those that have undergone some degree of aging. Sediments in the final age layer of surficial sediment have the lowest resuspension potential. Not all age layers within surficial sediment segments will necessarily hold sediment at all times during a simulation. Frequently, the oldest layer will hold most of the sediment mass.

As particles settle to surficial sediments, the particles enter the first (freshest) age layer of the surficial sediments and the volume (depth) of those segments increases. However, the particle concentration (density/porosity) in each surficial sediment segment is constant. At a user

specified sediment aging interval, particles are "moved" to the next (older) age layer. A typical sediment aging interval is 1 day. A typical number of sediment age layers is 7. If no new (fresh) sediment enters the segment, all particles within the segment will eventually enter the final (oldest) age layer (and all other layers will be empty). All particles in the final age layer have the same resuspension potential regardless of how long they have been in the layer. Users should be aware that particles are never transported to the subsurface sediments as a result of aging. Unless subsequently resuspended, particles will remain in the surficial sediments until burial occurs.

As particles are resuspended from surficial sediments, particles are removed from one or more age layers and the volume (depth) of those segments decreases. (Recall that the total particle concentration of the surficial sediments will be constant.) The particle mass removed from the surficial sediments as a result of resuspension will be equal to the amount ε (as computed from Equations 1.37 - 1.39), modified by the sediment age factor (Z) of the age layer from which resuspension is occurring. If the mass of sediment to be resuspended exceeds the mass present in an age layer, all particles in that layer are resuspended and the process proceeds with the next age layer, sequentially from freshest to oldest, until the proper particle mass is resuspended. During this process, several age layers may be temporarily unoccupied (empty) until particles enter the empty layers by settling and subsequent aging. However, IPX is designed so that if the mass of particles to be resuspended during any time-step exceeds the total mass present at that time, resuspension will stop (i.e. resuspension stops if the available supply of resuspendable sediments is exhausted). If at the end of any simulation time-step, the volume of any surficial sediment segment is less than the minimum volume (depth) condition, burial is automatically triggered.

The user should be aware that sediment age layers serve only to describe how the resuspension potential of sediments change with time. Age layers are *conceptual* divisions within a surficial sediment segment; the number of model segments is not affected by the number of age layers simulated in the sediments. For the purpose of computing a mass balance, the sediments in all age layers are considered. Alternatively stated, the sum of the sediment masses in the age layer equals the total sediment mass in the segment; the sum of the depths of the age layer equals the total depth, and therefore volume, of the segment. Particle concentrations in the surficial sediments are constant.

1.5.4.2 Subsurface Sediments

Eulerian Sediment Bed Option: For Eulerian representations of the sediment bed, burial computations are performed at a fixed time interval (regardless of sediment volume conditions)

as specified by the input variable TDINTS in Data Group C. The interval defined should be representative of the time required for physical, biological, and chemical processes, such as bioturbation and compaction, to change sediment properties. In addition, a minimum volume condition also exists for the Eulerian sediment bed option such that burial computations are performed whenever any surficial sediment segment is reduced to 25% of its initial volume. Any time burial computations are performed, the volumes of all surficial sediment segments are globally restored to their initial volumes. A description of burial computations for the Eulerian sediment bed option is presented in Section 1.5.3.

Whenever burial/scour occurs, particles and associated chemicals are transported through each subsurface sediment segment within a vertical stack under a given surficial sediment segment. If the volume of the surficial sediment segment at the top of the stack is greater than its initial volume, burial occurs and particles and chemicals are transported downward to the first subsurface sediment segment. However, the particle concentration and volume of each subsurface sediment segment are constant. An equal mass of particles, and the chemical mass associated with these displaced particles, is transported from the uppermost subsurface sediment segment, through each subsequent subsurface layer, and across the bottom boundary of the deepest subsurface sediment segment in the stack.

If the volume of the surficial sediment segment at the top of the stack is less than its initial volume, scour occurs and particles and chemicals are transported upward across the bottom boundary of the model into the deepest subsurface sediment segment of the stack. (Recall that the particle concentration and volume of each subsurface sediment segment are constant.) Particle and chemical concentrations at this and all other boundaries are specified by the user. **For the sediment bed, particle boundary conditions must be greater than zero.** Chemical boundary conditions for the sediments can have any positive value. **However, the model network should be developed so that chemical concentrations at the sediment boundary of the system are zero.** Users should be aware that **if the chemical sediment boundary condition is greater than zero, the boundary can act as an infinite source** of the chemical to the system. An equal mass of particles, and associated chemical mass, is then transported from the deepest subsurface sediment segment, through each overlying subsurface layer, and into the oldest age layer of the surficial sediment segment at the top of the stack.

Pore water and mobile-phase (dissolved and DOC-bound) chemicals are squeezed upward through the sediments and into the water column whenever burial or scour occur. Although the particle concentration and volume of each subsurface sediment segment remain

constant, chemical concentrations will vary during a simulation. If burial exceeds scour in the long term, chemical concentrations in the sediments will approach the chemical concentration on particles in the water column. Conversely, if scour exceeds burial, chemical concentrations in the sediments will approach the chemical concentration specified at the bottom boundaries of the model network.

Semi-Lagrangian Sediment Bed Option: For semi-Lagrangian representations of the sediment bed, burial computations (segment re-indexing) are performed when a surficial sediment segment reaches either the minimum or maximum volume (depth) conditions as specified by the input variables MINDEP and MAXDEP in Data Group L. The minimum volume condition for a stack is computed as the product of MINDEP and the initial volume of the surface sediment segment. Similarly, the maximum volume condition is computed as the product of MAXDEP and the initial volume of the surface sediment segment. The minimum and maximum volume conditions defined should be representative of the physical (and biological) processes that alter sediment properties and contaminant distributions over time. Burial computations are performed on an individual basis as each stack reaches a minimum or maximum volume conditions. A description of burial computations (push and pop) for the semi-Lagrangian sediment bed option is presented in Section 1.5.3.

Whenever burial (segment re-indexing) occurs, the identities and properties (volume, area, thickness (depth), state variable concentrations) of each segments in the sediment stack are exchanged. When the maximum volume condition is reached, the surficial sediment segment is split to become two segments. The upper portion of the split surface sediment segment becomes the new (smaller) surficial sediment segment, the lower portion of the split segment becomes the next segment in the stack, and all other segments (and ghosts) are pushed down the stack and re-indexed. The downward re-indexing of sediments is managed by Subroutine PUSH. When the minimum volume condition is reached, the residual volume of the surficial sediment segment (if any) is joined with the volume of the next element in the sediment stack (if that element is occupied) to become one segment. The joined segment becomes the surficial sediment segment and all other segments (and ghosts) are popped up the stack and re-indexed. The upward re-indexing of sediments is managed by Subroutine POP.

During the course of a simulation, the entire sediment stack at any location, including any ghost stack elements, can be empty (unoccupied). Conversely, the entire sediment stack and all ghost elements can be occupied. If downward re-indexing occurs at a locations where all elements of the stack are occupied, the simulation will proceed according to the ghost collapse

option. The ghost collapse option is set by the input variable IGOPT specified for that stack in Data Group L. A separate IGOPT value is specified for each sediment stack that uses the semi-Lagrangian sediment bed option. The ghost collapse option allows the bottom two ghost elements in a stack to merge to create an empty element in the stack prior to downward re-indexing. If IGOPT = 0, ghost stack elements do not collapse. When all stack elements are full, the next downward re-indexing event for that stack causes the simulation to abort and display a message indicating the location (surficial sediment segment number) and time that the condition occurred. If IGOPT = 1, the bottom two ghost elements of the sediment stack merge to form a single (larger) ghost. When all stack elements are full, the next downward re-indexing event for that stack causes the bottom two ghosts to merge and the simulation continues. Subsequent downward re-indexing events result in further ghost collapse and the (potentially infinite) growth of the collapsing ghost element at the bottom of the sediment stack. Regardless of the value of the ghost collapse option, **mass is never transported out of or into the model network across the bottom barrier of a sediment stack** using the semi-Lagrangian sediment bed option.

1.5.5 Screening-Level IPX Sediment Transport Simulation Guidelines

1. Resuspension events are defined by the hydrograph. These events can occur at random but typically occur with greater frequency in the Spring and Fall. The duration of resuspension events is a function of the hydrograph, starting when flows begin to increase, through the flow peak, and continuing until flows decrease to base levels. Depending on the system, events can last from a few days (or less) to several weeks or even months.

2. High flow events disturb the sediments and alter their resuspension properties. Following a resuspension event, physical, chemical, and biological processes restore sediment resuspension properties to their typical values in 30 days. Additional high flow events (peak flow must exceed the previous peak) that occur within this 30 day window should be treated as continuations of the first event of the series that disturbed the sediments. The sediments return to their typical resuspension properties in 30 days following the last peak (highest overall flow).

3. Settling velocities of medium-grained, cohesive particles may vary by season. During Winter, when particles are largely inorganic, settling velocities are greatest. During Summer, when particles are most organic (biotic), the settling velocities are smallest. During Spring and Fall, settling velocities are somewhere between the Winter and Summer values.

4. Background resuspension of fine-grained sediments occurs because these materials are kept in a quasi-disturbed state by water flowing over or through the surficial sediments. In fast-moving river reaches where coarser-grained materials predominate, background resuspension is minimal (less than in slower reaches) because fine-grained materials do not accumulate there (i.e. are not available for resuspension) and under non-event conditions coarse-grained materials do not easily resuspend.

5. The extent of apparent background resuspension may vary by river reach and by season as a function of local water velocity/shear stress differences. Background resuspension may be greater in high velocity reaches and during the Spring and Fall when flows tend to be larger.

6. High velocity river reaches have less cohesive sediments available for resuspension so sediments in these reaches are more difficult to resuspend (greater Z and/or lower m values).

7. Easily resuspendable surficial sediments may build up over the Winter under ice-cover. The first resuspension event in the Spring after ice-off may be strongly influenced by these easily resuspendable sediments (smaller Z values in the early Spring for river reaches were sediments may accumulate).

8. In areas where non-cohesive sediments predominate (often narrow, high velocity river reaches) resuspension reaches its maximum rapidly but returns to background levels more slowly than do areas with predominantly cohesive sediments (i.e. considerable erosion continues during the declining limb of an event because non-cohesive sediments do not armor to the extent that cohesive sediments do).

9. Substantial deposition can occur following the peak of a resuspension event as particles are removed from the water column by settling. In regions where sediment accumulate, the sediments may be relatively uncompacted and more resuspendable for a short period until compaction or other processes occur that restore sediment properties to their typical values (smaller Z and/or τ_c values for up to 30 days).

1.6 SIMULATING THE TRANSPORT AND FATE OF TOXIC CHEMICALS USING IPX

In addition to physical transport due to the movement of water, physical, chemical, and biological mass transfer and transformation processes can affect the transport and fate of toxic chemicals in the aquatic environment. As presented in Figure 1.5. the transport and fate

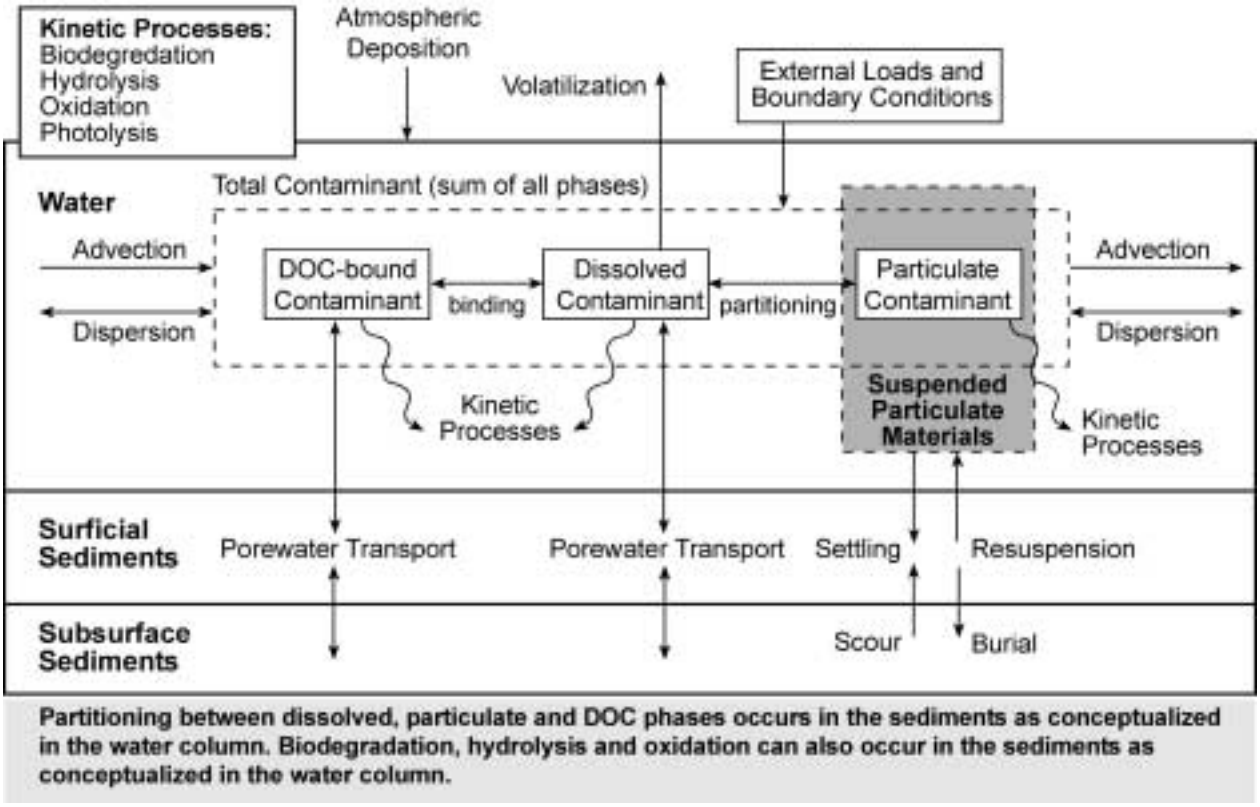


Figure 1.5. Mass transport, transfer and transformation processes in IPX.

processes that can be simulated are: advection, dispersion, settling, resuspension, burial (scour), sediment pore water advection and diffusion, multi-phase partitioning (water, solids, and dissolved organic materials), volatilization, photolysis, hydrolysis, oxidation, biodegradation, and external loadings. IPX also allows an additional, user defined "extra" reaction to be specified. In addition to these processes, appropriate treatment of external loads (including atmospheric deposition) and boundary conditions is necessary for a complete and accurate description of toxicant transport and fate. Chapra (1997), Thomann and Mueller (1987), Chapra and Reckhow (1983), and Mackay and Paterson (1986) offer procedures for specifying these data. For reference, concentration related symbols are defined in Table 1.5.

IPX allows the user to simulate the transport of one to three types of solids (particulate materials) and the transport and transformation of any number of chemicals. The simulated

Table 1.5. Concentration related symbols used in mathematical equations.

Symbol	Definition	Units
C_j	Concentration of total chemical in segment j.	mg_c/L
C_{wj}	Concentration of dissolved chemical in segment j.	mg_c/L
C'_{wj}	Concentration of dissolved chemical in water in segment j on a water volume basis.	mg_c/L_w
C_{sj}	Concentration of chemical sorbed to sediment type s in segment j.	mg_c/L
C'_{sj}	Concentration of chemical sorbed to sediment type s in segment j on a mass basis ($C'_{sj} = C_{sj}/M_{sj}$).	mg_c/kg_s
C_{Bj}	Concentration of DOC-bound chemical in segment j.	mg_c/L
C'_{Bj}	Concentration of DOC-bound chemical in segment j on a mass basis ($C'_{Bj} = C_{Bj}/B_j$).	mg_c/kg_b
m_{sj}	Concentration of sediment type s in segment j.	mg_s/L
M_{sj}	Concentration of sediment type s in segment j ($M_j = m_j/10^6$).	kg_s/L
M'_{sj}	Concentration of sediment type s in water in segment j ($M'_{sj} = M_{sj}/n_j$).	kg_s/L_w
B_j	Concentration of DOC in segment j.	kg_b/L
B'_j	Concentration of DOC in water in segment j.	kg_b/L_w
n_j	Porosity of segment j ($V_{water}/V_{water + solids}$).	L_w/L
K_{ps}	Partition coefficient of chemical for sediment type s.	L_w/kg_s
K_B	DOC-binding coefficient of chemical.	L_w/kg_b

chemicals may be independent, such as different pesticides or coupled by reaction pathways and yields, such as a parent compound-daughter product sequence. Users should be aware that unlike WASP4 (TOXI4), IPX does not simulate ionic speciation. Chemicals can exist in five phases: dissolved, bound to dissolved organic carbon (DOC), and sorbed to each of the three possible solids types that can be simulated. Local equilibrium is assumed and the distribution of the chemical between each phase is defined by partition coefficients. The concentration of a chemical in any phase can be computed from the total concentration of the chemical.

In the aquatic environment, chemicals may be transferred between media (air, water, and solids) and may be transformed by a number of physicochemical and biological processes. Defined mass transfer processes include sorption (equilibrium partitioning) and volatilization. Transformation processes include biodegradation, hydrolysis, photolysis, and oxidation. Sorption is treated as an equilibrium partitioning process. All mass transfer and transformation

processes are described by rate equations. Rate equations may be quantified by first-order reaction constants or by second-order, chemical-specific and environment-specific reaction constants that may vary in space and time.

IPX uses a finite difference form of Equation 1.2 (presented in more detail as Equations 1.124 and 1.125) to calculate sediment and chemical mass and concentrations for every segment in a specialized network that may include surface water, underlying water, surface bed, and underlying bed. In a simulation, sediment is treated as a conservative constituent that is advected and dispersed through water segments, settles to and resuspends from surficial sediment segments, and moves between surficial and subsurface sediment segments burial, unburial, or bed load.

During a simulation, chemicals can undergo several physical, chemical, or biological transformations. It is convenient to group these into fast and slow reactions. Fast reactions have characteristic reaction times on the same order as the model time-step and are handled with the assumption of local equilibrium. Slow reactions have characteristic reaction times much longer than the model time-step. These are handled with the assumption of local first-order kinetics using a lumped rate constant specified by the user, or calculated internally, based on summation of several process rates, some of which are second-order. Thus, the effective first-order decay rate can vary with time, and space, and is recalculated as often as necessary throughout a simulation. The chemical is advected and dispersed among water segments, and exchanged with surficial benthic segments by dispersive mixing. Sorbed chemical settles through water column segments and deposits to or erodes from surficial benthic segments. Within the bed, dissolved chemical migrates downward or upward through percolation and pore water diffusion. Sorbed chemical migrates downward or upward through net sedimentation or erosion. Both rate constants and equilibrium coefficients must be estimated in most toxic chemical studies. Although these can be calculated internally from chemical properties and local environmental characteristics, site-specific calibration or testing is desirable.

One important limitation should be kept in mind when developing simulations: chemical concentrations should be near trace levels. A good guideline is that concentrations should be less than half the chemical solubility limit. At higher concentrations, the assumptions regarding linear partitioning and other transport and fate processes may not apply. Also, at very high concentrations, chemical density may become important, particularly near the chemical source; such might be the case when simulating a chemical spill. Extremely high concentrations can

affect key environmental characteristics such as pH or bacterial populations, thereby altering transformation rates. IPX does not allow simulation of such feedback phenomena.

1.6.1 Equilibrium Sorption

Dissolved chemicals in the water column and sediments interact with particles and non-filterable organic materials, conceptualized as dissolved organic carbon or DOC, to form five phases: dissolved, DOC-bound, and sediment-sorbed (particulate) to each of the three possible sediment types ("s"). These interactions can be written with respect to a unit volume of water:

$$M_s^{'} + C_w^{'} \Leftrightarrow \frac{C_s}{n} \tag{1.41}$$

$$B^{'} + C_w^{'} \Leftrightarrow \frac{C_b}{n} \tag{1.42}$$

For particles, the forward reaction is sorption and the reverse reaction is desorption. For DOC, the forward reaction is binding and the reverse reaction is unbinding. These reactions are usually fast in comparison with the model time-step, and can be considered in local equilibrium. The phase concentrations C_W, C_S, and C_B are governed by the equilibrium partition and binding coefficients K_{ps0} and K_B (L/kg):

$$K_{ps0} = \frac{C_s / n}{M_s^{'} C_w^{'}} = \frac{C_s^{'}}{C_w^{'}} \tag{1.43}$$

$$K_B = \frac{C_B / n}{B^{'} C_w^{'}} = \frac{C_B^{'}}{C_w^{'}} \tag{1.44}$$

These equations give the linear form of the Freundlich isotherm, applicable when sorption/binding sites on sediment and DOC are plentiful:

$$C_s^{'} = K_{ps} C_w^{'} \tag{1.45}$$

$$C_B^{'} = K_B C_w^{'} \tag{1.46}$$

The partition and binding coefficients depend upon characteristics of the chemical and the sediments or DOC to which partitioning occurs. Many pollutants of public health interest are non-polar, hydrophobic, organic compounds. The partition and binding coefficients of these compounds correlate well with the organic carbon fraction (f_{oc}) of the sediment. Rao and Davidson (1980) and Karickhoff et al. (1979) developed empirical expressions relating

equilibrium coefficients to laboratory measurements, leading to fairly reliable means of estimating appropriate values. Conceptually, dissolved organic materials are composed entirely of organic carbon ($f_{oc} = 1$). However, measured DOC-binding constants are generally one to two orders of magnitude smaller than predicted (Eadie et al. 1990; Landrum et al. 1985; Landrum et al. 1987; Capel and Eisenreich, 1990), suggesting that not all non-filterable material measurable as organic carbon is available for binding. The partitioning and binding expressions used in IPX are:

$$K_{ps0} = f_{ocs} K_{oc} \tag{1.47}$$

$$K_B = D_E f_{ocs} K_{oc} \tag{1.48}$$

where: K_{oc} = organic carbon partition coefficient, L_w/kg_{oc} [L^3/M]
f_{ocs} = organic carbon fraction of sediment or DOC
D_E = DOC-binding effectiveness constant = 0.01 - 0.1

If no K_{oc} values are available, a value can be generated internally from the octanol-water partition coefficient (K_{ow}) (L_w/L_{oct}) using the following correlation:

$$\boldsymbol{log}\, K_{oc} = a_0 + a_1 \boldsymbol{log}\, K_{ow} \tag{1.49}$$

If a_0 and a_1 are not specified, default values of *log* 0.6 (-0.2218) for a_0 and 1.0 for a_1 are used.

The value of the partition coefficient depends on numerous factors in addition to the fraction organic carbon of the sorbing/binding matrix. Of these, perhaps the most potentially significant and the most controversial is the effect of particle concentration, which was first presented by O'Connor and Connolly (1980). Based on empirical evidence, O'Connor and Connolly concluded that the partition coefficient was inversely related to the particle concentration. Much research has been conducted to prove or disprove this finding. At present, the issue remains contentious. A particle interaction model has been proposed (Di Toro, 1985) which describes the effects of particle concentration. This model was shown to be in conformity with observations for a large set of adsorption-desorption data. The expression defining the partition coefficient is:

$$K_{ps} = \frac{K_{ps0}}{1 + M_s K_{ps0} / \nu_x} \tag{1.50}$$

where: K_{ps0} = limiting partition coefficient with no particle interaction = f_{ocs} K_{oc}, L/kg [L^3/M]

M_s = solids concentration, kg/L [M/L^3]

ν_x = particle interaction parameter = the ratio of adsorption to particle-induced desorption rate

Di Toro found that ν_x was of order 1 over a broad range of chemical and solids types. This formulation is included in IPX. The user may include the effect of particle concentration on adsorption by using a ν_x value of order 1 (see Di Toro, 1985 for more detail); the effect may be eliminated by specifying a large value for ν_x (the default value is 10^{12}). If ν_x is specified to be 1.0, the model will predict a maximum particulate fraction in the water column of 0.5 for all hydrophobic chemicals (K_{ps0} M_s > 10).

For each chemical modeled, up to 5 partition coefficients can be defined representing the dissolved and four sorbents (DOC and three types of solids) states. Sorption/binding of the chemical to solids and DOC is defined by the f_{oc} of the sorbent (assumed to be 1 for DOC but modifiable through selection of other model parameters), the organic carbon partition coefficient of the chemical (K_{oc}), or the user defined relationship between K_{ow} and K_{oc}, and the particle interaction parameter ν_x value.

The total chemical concentration is the sum of the five phase concentrations:

$$C = C_w' n + \sum C_s' M_s + C_B' B \tag{1.51}$$

Substituting Equations 1.47 and 1.48 into Equation 1.51, factoring, and rearranging terms, yields the dissolved fraction f_d:

$$f_d = \frac{C_w' n}{C} = \frac{1}{1 + K_B B' + \sum K_{ps} M_s'} \tag{1.52}$$

Similarly, the particulate (sediment-sorbed) and DOC-bound fractions are:

$$f_{ps} = \frac{C_s' M_s}{C} = \frac{K_{ps} M_s'}{1 + K_B B' + \sum K_{ps} M_s'} \tag{1.53}$$

$$f_b = \frac{C_B' B}{C} = \frac{K_B B'}{1 + K_B B' + \sum K_{ps} M_s'} \tag{1.54}$$

These fractions are determined in time and space throughout a simulation from the partition coefficients, internally calculated porosities, simulated sediment concentrations, and specified DOC concentrations.

Given the total concentration and the five phase fractions, the dissolved, sorbed, and bound concentrations are uniquely determined:

$$C_w = f_d C \tag{1.55}$$

$$C_s = f_{ps} C \qquad \text{(for each possible solids type "s")} \tag{1.56}$$

$$C_b = f_b C \tag{1.57}$$

These five concentrations have units of mg/L, and can be expressed as concentrations within each phase:

$$C'_w = \frac{C_w}{n} \tag{1.58}$$

$$C'_s = \frac{C_s}{M_s} \tag{1.59}$$

$$C'_B = \frac{C_B}{B} \tag{1.60}$$

These concentration expressions have units of mg/L_w, mg/kg_s, and mg/kg_B, respectively.

In some cases, such as near discharges, the user may have to alter input partition coefficients to describe the effect of incomplete (non-equilibrium) partitioning. As guidance, Karickhoff and Morris (1985) found that typical sorption reaction times are related to the partition coefficient:

$$\frac{1}{k_d} = 0.03 K_{ps} \tag{1.61}$$

where: k_d = desorption rate constant, hr [T]

Table 1.6. IPX partitioning/binding data.

Description	Notation	Common Range	S. I. Units
Suspended solids concentration	m_s	10 - 100	mg/L
Sediment bed solids concentration	M_B	0.5 - 2	kg/L
Dissolved organic carbon	DOC, B	0 - 10	mg/L
Partition coefficient, phase i	K_{pi}	10^{-1} - 10^{5}	L/kg
Lumped metal distribution coefficient	K_D	10^{0} - 10^{5}	L/kg
Octanol-water partition coefficient	K_{ow}	10^{0} - 10^{6}	-
Organic carbon fraction, phase i	f_{oci}	0.005 - 0.5	-
Particle interaction parameter	ν_x	1 - 10^{12}	-

Thus, compounds with high, medium, and low K_{ow} values of 10^5, 10^3, and 10 sorbing onto 2% organic sediment should have reaction times of 1 day, 1/2 hour, and seconds. Given that the time to equilibrium is roughly three times the reaction time, the three compounds should reach equilibrium within 3 days, 1 hour, and 30 minutes. IPX data specifications for partitioning/binding are summarized in Table 1.6.

1.6.2 Kinetic Transformations

The various phases of a chemical in water column and sediment segments are subject to several transformation processes. Several variables may influence each process, leading to a multi-term, and often non-linear, lumped transformation rate. If a single process is dominant in a homogeneous aquatic system, then a single rate constant may be sufficient to describe the kinetic reaction:

$$S_{kc} = -K_{kc} C \tag{1.62}$$

where: S_{kc} = total kinetic transformation rate for chemical c g/m3-day [$M/L^3/T$]
K_{kc} = first-order rate constant for process k, day-1 [1/T]
C = total concentration of chemical, mg/L (g/m3) [M/L^3]

Reaction can also be specified by a half-life. If a half-life is entered, then it will be converted to a rate constant:

$$K_{kc} = \frac{0.693}{t_{Hkc}} \tag{1.63}$$

If multiple rate constants are entered, they are summed:

$$S_{kc} = -\sum_{k} K_{kc} C \tag{1.64}$$

For nonhomogeneous aquatic systems where rates vary in space, the user may specify a spatially variable, lumped first-order rate constant $K_{Tc}(x)$, so that:

$$S_{kc} = -K_{Tc}(x) C \tag{1.65}$$

For nonhomogeneous aquatic systems where rates may vary in space and time, or for cases where rate constants are unknown or cannot be calibrated, IPX uses the strategy implemented in the original Exposure Analysis Modeling System (Burns et al. 1982). Each process is considered separately using mixed second-order kinetics:

$$C + [E]_k \Rightarrow P_{kc} \tag{1.66}$$

where: $[E]_k$ = the intensity of environmental property "E" that affects process "k", such as light intensity or bacterial population

P_{kc} = transformation product for process k acting on chemical c

The corresponding reaction rate S_{kc} in mg/L-day for process k acting on chemical c is:

$$S_{kc} = k_{kc} [E]_k Y_{kc} C \tag{1.67}$$

where: k_{kc} = second-order rate constant for process k on chemical c

Y_{kc} = yield coefficient for production of chemical from process k acting on chemical c; assumed to be -1 for the production of chemical c by itself

Given a local value for $[E]_k$, a pseudo-first-order rate coefficient K_{kc} in day^{-1} can be specified:

$$K_{kc} = k_{kc} [E]_k Y_{kc} \tag{1.68}$$

For a compound undergoing several reactions, the lumped transformation reaction is:

$$S_T = \sum_{k} \sum_{c} S_{kc} \tag{1.69}$$

Table 1.7. IPX general kinetic data.

Description	Notation	Range	Units
First-order rate constant for process "k"	K_k	0 - 10	day^{-1}
Half-life for process "k"	t_{Hk}	0.07 - ∞	days
Lumped first-order rate constant	K_T	0 - 10	day^{-1}
Chemical solubility	Sol	10^{-6} - 10^{6}	mg/L
Water temperature	T	4 - 30	°C

The local first-order assumption is generally accepted to be accurate for most chemicals at environmental concentrations. The assumption is invalid at concentrations near the solubility limit, however. If the user does not specify a maximum concentration CMAX(1), IPX sets this limit at half the solubility or 10^{-5} molar, whichever is less, and aborts the simulation if concentrations exceed this value.

The individual transformation processes considered by IPX are hydrolysis, photolysis, oxidation, and biodegradation. In addition, volatilization is calculated and added to the transformation rate. Good discussions of these processes are presented in Smith et al. (1977), Burns et al. (1982), Mill et al. (1982), Mabey et al. (1982), Mills et al. (1985), and others. The following sections summarize how IPX calculates the local rate constant for each of these processes. Input data requirements are given for each process. The general kinetic data required by IPX are summarized in Table 1.7.

1.6.3 Hydrolysis

Hydrolysis, the reaction of a chemical with water, is a major degradation pathway for many toxic organic contaminants. An example reaction is shown in Figure 1.6. The reaction can be catalyzed by hydrogen ions or proceed by consuming hydroxide ions. Figure 1.7. illustrates the effects of pH on the base hydrolysis of carbaryl, the neutral hydrolysis of chloromethane, and the acid and base hydrolysis of 2,4-D.

In IPX, hydrolysis by specific acid, neutral, or base-catalyzed pathways is considered for the various phases of each chemical:

$$K_{HN} = \sum_j k_{nj} f_j \tag{1.70}$$

$$K_{HH} = \sum_j k_{aj} \left[H^+\right] f_j \tag{1.71}$$

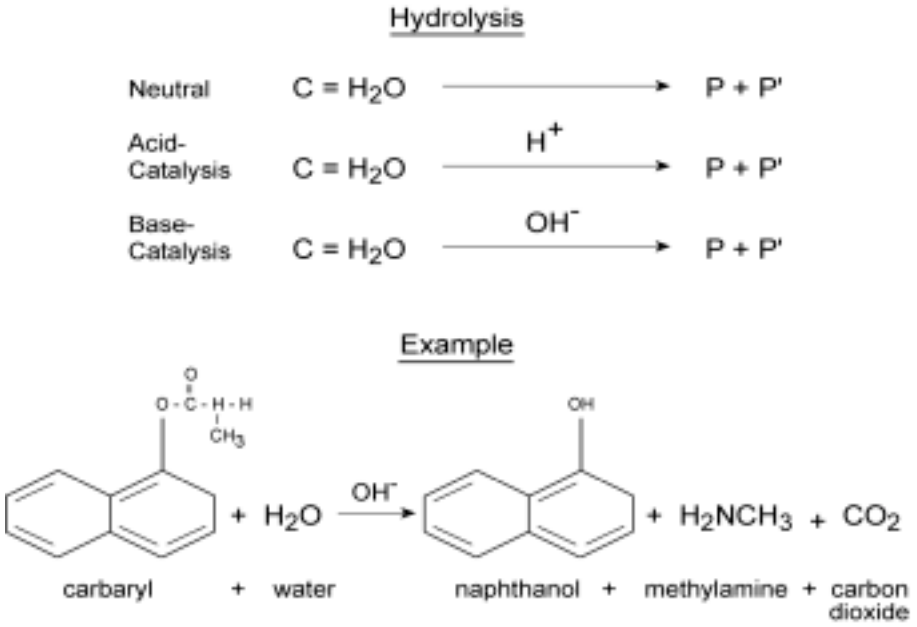


Figure 1.6. Hydrolysis reactions.

$$K_{HOH} = \sum_j k_{bj} \left[OH^-\right] f_j \tag{1.72}$$

where: K_{HN} = neutral hydrolysis rate constant, day^{-1} [1/T]
K_{HH} = acid catalyzed hydrolysis rate constant, day^{-1} [1/T]
K_{HOH} = base catalyzed hydrolysis rate constant, day^{-1} [1/T]
k_{aj}, k_{bj} = specific acid catalyzed (a) and base (b) rate constants for chemical in phase j, molar^{-1} day^{-1} [L^3/moles/T]
k_{nj} = neutral rate constant for chemical in phase j, day^{-1} [1/T]
f_j = fraction of chemical in phase j

IPX hydrolysis data specifications are summarized in Table 1.8. The reaction coefficients can be specified as constants, with activation energy constants left as 0. If non-zero activation energies are specified, IPX can compute the rates based on the temperature-based Arrhenius function for each rate constant k_H as follows:

$$k(T_k) = k(T_R) e^{\left[1000 E_{aH} (T_k - T_R) / (R T_k T_R)\right]} \tag{1.73}$$

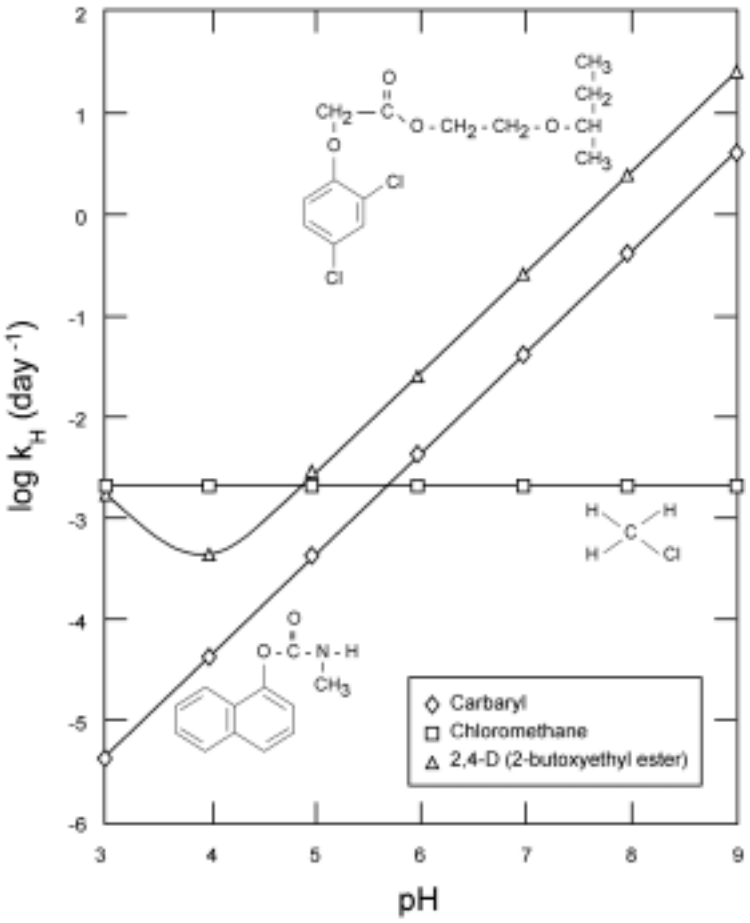


Figure 1.7. pH dependence of example hydrolysis reactions.

where: T_k = water temperature, K
T_R = reference temperature for which reaction rate is reported, K
E_{aH} = Arrhenius activation energy for hydrolysis reaction, kcal/mole
R = 1.99 cal/mole K
1000 = cal/kcal

Activation energies may be specified for each hydrolysis reaction (acid, neutral, base) simulated. If activation energies are input, reaction rates are adjusted to ambient water temperatures. If no activation energies are specified, then rate constants are not adjusted for temperature.

Table 1.8. IPX Hydrolysis Data

Description	Notation	Range	Units
Negative *log* of hydrogen ion activity [H^+]	pH	5 - 9	-
Acid hydrolysis rate constant chemical in phase j	k_{HAj}	0 - 10^7	$\frac{kcal}{mole[H^+]°C}$
Neutral hydrolysis rate constant for chemical in phase j	k_{HNj}	0 - 10^2	day^{-1}
Base hydrolysis rate constant for chemical in phase j	k_{HBj}	0 - 10^7	$\frac{kcal}{mole[OH^-]°C}$
Water temperature	T	4 - 30	°C
Activation energy for hydrolysis reaction for chemical	E_{aH}	15 - 25	$\frac{kcal}{mole°C}$

1.6.4 Photolysis

Photolysis is the transformation of a chemical due to absorption of light energy. An example of several photochemical pathways is given in Figure 1.8. The first-order photolysis rate at the water surface can be calculated as:

$$k_{ps} = \phi \sum_k \varepsilon_k L_k \qquad (1.74)$$

where: k_{ps} = first-order photolysis rate coefficient at the water surface, day^{-1} [1/T]

ϕ = reaction quantum yield for chemical, mole/E
(E is Einstein, a molar unit for light)

ε_k = extinction coefficient of wavelength k by chemical, 1/M/cm

L_k = average light intensity of wavelength k, $mE/cm^2/day$

Usually, k_{ps} (or, preferrably ε_k and ϕ) is treated as a reference rate in the literature and chemical databases. Adjustment to the water body and conditions of interest is made in the computation of the depth-integrated photolysis rate constant, k_p.

The rate of photolysis over the depth of the water column depends upon the attenuation of light in water. For many organic chemicals, light absorption occurs primarily in the UV-B wavelengths (280-320 nm), which are strongly attenuated by water as well as dissolved organic matter. As a result, essentially all photolysis takes place in the upper meter of the water column.

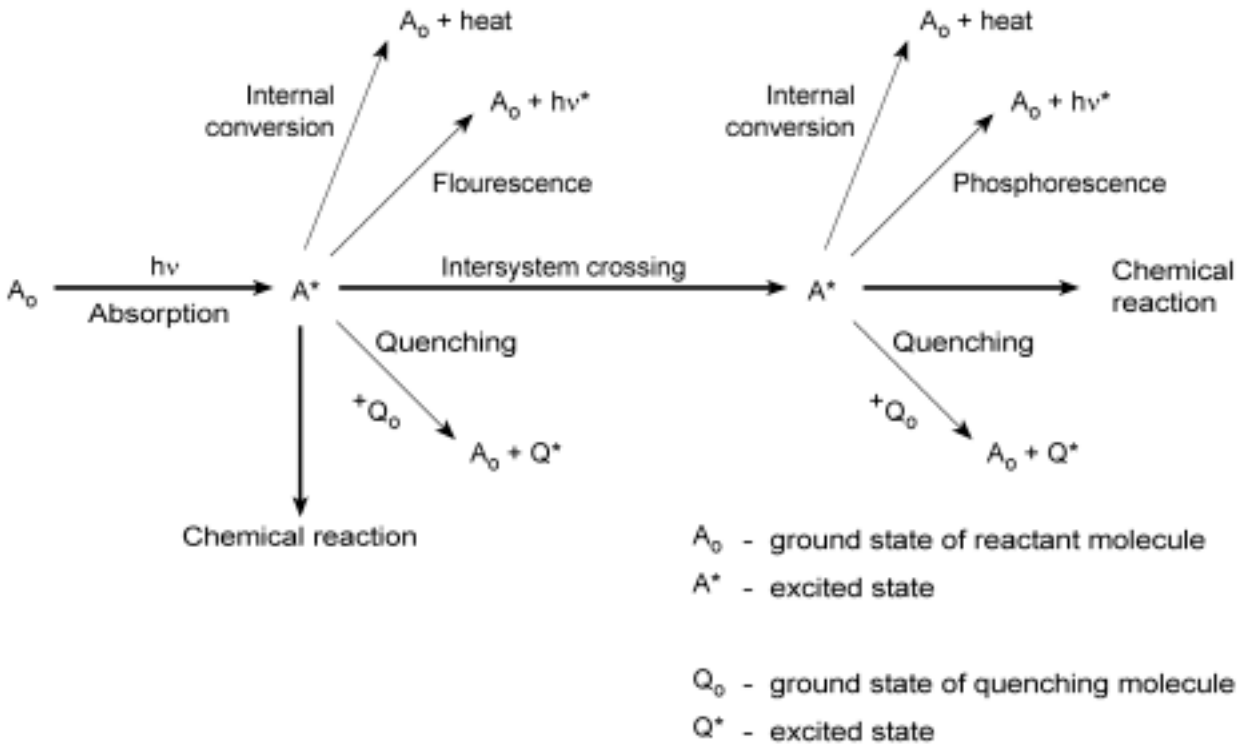


Figure 1.8. Photolysis reactions.

It may then be assumed that all of the light is absorbed in the surficial water column segments, for which the depth-integrated photolysis rate constant can be calculated as:

$$k_p = \phi \sum_k \frac{\varepsilon_k L_k}{\alpha_k} \qquad (1.75)$$

where: k_p = depth-integrated photolysis rate, m/day [L/T]
α_k = light attenuation coefficient at wavelength k, m^{-1} [1/L]

For UV-B wavelengths, representative measurements of α_k are 1/m for large water bodies such as the Great Lakes (Calbins, 1975; personal communication, T. Mill, SRI), and 10/m for rivers in the southeastern U.S. (Zepp and Cline, 1977).

Adjustment of k_p for the difference in latitude between the water body of interest and the reference location is made by a latitude correction factor:

$$latc = \frac{191696.65 + 87054.63\,\boldsymbol{cos}\left(0.0349\,Lat\right)}{191696.65 + 87054.63\,\boldsymbol{cos}\left(0.0349\,Lat_{ref}\right)} \tag{1.76}$$

where: Lat = latitude of water body of interest (°N)
Lat_{ref} = reference latitude for measured or calculated k_p (°N)

Adjustment of k_p for the variation in light intensity due to season and cloud cover may also be made. Table 1.9 presents mid-season values of L_k, which incorporate diurnal photoperiod, solar declination, and spectral intensity, calculated for a latitude of 40° N (personal communication, T. Mill, SRI). The effect of cloud cover upon the rate of photolysis may be estimated by a cloud cover intensity reduction factor:

$$C_R = \left(1 - 0.5 f_{cc}\right) \tag{1.77}$$

where: C_R = cloud cover intensity reduction factor
f_{cc} = fractional cloud cover

IPX photolysis data specifications are summarized in Table 1.10. In IPX, the user specifies the annual average, depth-integrated photolysis rate k_p, which can be calculated using Equation 1.75. In addition to the adjustments for latitude correction and cloud cover, the time function PHTON can be used to adjust the photolysis rate to represent seasonal changes in light intensity. Finally, the quantum yield fractions F_j are specified to indicate which chemical phase(s) (dissolved, DOC-bound, and particle-sorbed fractions) are subject to photolysis. The overall first-order, depth-integrated photolysis rate constant for surface water segments is computed as:

$$K_{PG} = PHTON \frac{k_p}{D} \sum_j F_j f_j \tag{1.78}$$

where: K_{PG} = surficial segment photolysis rate, day^{-1} [1/T]
PHTON = time function to seasonally adjust annual average photolysis rate
D = depth of surface water segment, meters [L]
F_j = quantum yield fraction for chemical in phase j
f_j = fraction of chemical in phase j

Table 1.9. Average light intensity L_k of wavelength k at 40°N, mE/cm^2/day.

Wavelength (nm)	Spring	Summer	Fall	Winter
297.5	1.85E-05	6.17E-05	7.83E-06	5.49E-07
300	1.06E-04	2.69E-04	4.76E-05	5.13E-06
302.5	3.99E-04	8.30E-04	1.89E-04	3.02E-05
305	1.09E-03	1.95E-03	5.40E-04	1.19E-04
307.5	2.34E-03	3.74E-03	1.19E-03	3.38E-04
310	4.17E-03	6.17E-03	2.19E-03	7.53E-04
312.5	6.51E-03	9.07E-03	3.47E-03	1.39E-03
315	9.18E-03	1.22E-02	4.97E-03	2.22E-03
317.5	1.20E-02	1.55E-02	6.57E-03	3.19E-03
320	1.48E-02	1.87E-02	8.18E-03	4.23E-03
323.1	2.71E-02	3.35E-02	1.51E-02	8.25E-03
330	9.59E-02	1.16E-01	5.44E-02	3.16E-02
340	1.23E-01	1.46E-01	7.09E-02	4.31E-02
350	1.37E-01	1.62E-01	8.04E-02	4.98E-02
360	1.52E-01	1.79E-01	9.02E-02	5.68E-02
370	1.63E-01	1.91E-01	9.77E-02	6.22E-02
380	1.74E-01	2.04E-01	1.05E-01	6.78E-02
390	1.64E-01	1.93E-01	9.86E-02	6.33E-02
400	2.36E-01	2.76E-01	1.42E-01	9.11E-02
410	3.10E-01	3.64E-01	1.87E-01	1.20E-01
420	3.19E-01	3.74E-01	1.93E-01	1.24E-01

Table 1.10. IPX photolysis data.

Description	Notation	Range	Units
Depth-integrated chemical photolysis rate	k_p	0-10	m/day
Reaction quantum yield fraction for chemical in phase j	F_j	0-1	

A much more sophisticated and elaborate algorithm, based upon EXAMS II (Burns and Cline, 1985), was used to calculate near-surface and depth-integrated photolysis rates in the WASP4 (TOXI4) framework. Substitution of the algorithm described in this section, was motivated by the desire for a simpler, more readily verified method to estimate photolysis rates than the EXAMS-based code found in the early version of WASP4 that served as the foundation for IPX. The authors hope to restore this algorithm in a later version of the IPX framework.

1.6.5 Oxidation

Chemical oxidation of chemicals in aquatic systems can be caused by interactions between free radicals and the pollutant. Free radicals can be formed as a result of photochemical reactions. Free radicals that have received some attention in the literature include alkylperoxy radicals, RO_2, hydroxide radicals, OH^-, and singlet oxygen, O.

In IPX, oxidation is modeled as a general second-order process for the various phases of each chemical:

$$K_o = [RO_2] \sum_j k_{oj} f_j \qquad (1.79)$$

where: Ko = net oxidation rate constant, day^{-1} [1/T]
$[RO_2]$ = molar concentration of oxidant, moles/L $[M/L^3]$
k_{oj} = second-order oxidation rate constant for chemical in phase j, L/mole-day $[L^3/M/T]$

The reaction coefficients may be specified as constants, with activation energy constants left (default value) as 0. If non-zero activation energies are specified, IPX can compute the rates based on the temperature-based Arrhenius function for each rate constant k_o as follows:

$$k(T_k) = k(T_R) e^{[1000 E_{ao}(T_k - T_R)/(RT_k T_R)]} \qquad (1.80)$$

where: E_{ao} = Arrhenius activation energy for oxidation reaction, kcal/mole

Activation energies may be specified for each chemical simulated. If no activation energies are given, then rate constants will not be adjusted to ambient water temperatures.

Because of the large number of alkylperoxy radicals that potentially exist in the environment, it would be impossible to obtain estimates of k_o for each species. Mill et al. (1982) propose estimation of a rate coefficient using t-butyl hydroperoxide as a typical oxidizing agent.

Table 1.11. IPX oxidation data.

Description	Notation	Range	Units
Oxidation rate constant for chemical phase j	K_o		L/mole-day
Activation energy for oxidation of chemical	E_{ao}	15 - 25	kcal/mole
Water temperature	T	4 - 30	°C
Concentration of oxidants	$[RO_2]$	10^{-17} - 10^{-8}	moles/L

Mill et al. argue that other alkylperoxides exhibit similar reactivities to within an order of magnitude. The second-order rate coefficients are specified in IPX as constants.

In addition to estimating a rate coefficient, estimates of free radical concentrations must be made to completely define the expression for free radical oxidation. Mill et al. (1982) reported RO_2 concentrations on the order of 10^{-9} M and OH^- concentrations on the order of 10^{-17} M for a limited number of water bodies. Zepp and Cline (1977) reported an average value on the order of 10^{-12} M for singlet oxygen in water bodies sampled. The source of free radicals in natural waters is photolysis of naturally occurring organic molecules. If a water body is turbid or very deep, free radicals are likely to be generated only near the air-water interface, and consequently, chemical oxidation will be relatively less important. In such cases, the concentrations cited above are appropriate in only the near-surface zones of water bodies. The molar oxidant concentrations are input to IPX using the parameter OXRADG(ISEG). IPX oxidation data specifications are summarized in Table 1.11.

1.6.6 Bacterial Degradation

Bacterial degradation, sometimes referred to as microbial transformation, biodegradation, or biolysis, is the breakdown of a compound by the enzyme systems in bacteria. Examples are given in Figure 1.9. Although these transformations can detoxify and mineralize toxins and defuse potential toxins, they can also activate potential toxins.

Two general types of biodegradation are recognized: growth metabolism and co-metabolism. Growth metabolism occurs when the organic compound serves as a food source for the bacteria. Adaptation times from 2 to 20 days were suggested by Mills et al. (1985). Adaptation may not be required for some chemicals or in chronically exposed environments. Adaptation times may be lengthy in environments with a low initial density of degraders (Mills et al. 1985). For situations where biodegradation is limited by the population size of the

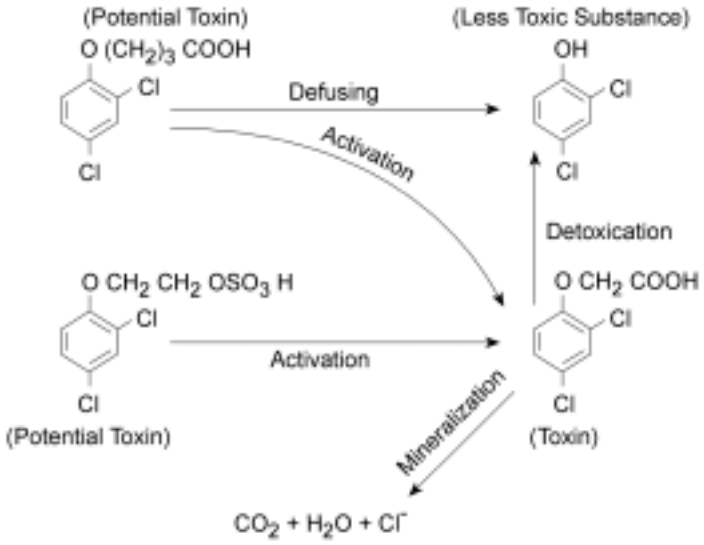


Figure 1.9. Example microbial transformations (from Alexander, 1980).

microorganism responsible for degradation, adaptation is faster for high initial microbial populations and slower for low initial populations. Following adaptation, biodegradation proceeds at fast, first-order rates. Co-metabolism occurs when the organic compound is not a food source for the bacteria. Although adaptation is seldom necessary, transformation rates are slow compared with growth metabolism.

In IPX, first-order biodegradation rate constants or half-life for the water column and the benthos may be specified. If these rate constants have been measured under similar conditions, this first-order approach is likely to be as accurate as more complicated approaches. If first-order rates are unavailable, or if they must be extrapolated to different bacterial conditions, then the second-order approach may be used. It is assumed that bacterial populations are unaffected by the presence of the compound at low concentrations. Second-order kinetics for chemical in the water column and the bed are considered:

$$K_{Bw} = P_{bac}(t)\sum_j k_{Bwj} f_j \tag{1.81}$$

$$K_{Bs} = P_{bac}(t)\sum_j k_{Bsj} f_j \tag{1.82}$$

Table 1.12. IPX Biodegradation Data.

Description	Notation	Common Range	Units
Observed first-order degradation rate in water column	K_{Bw}	0 - 0.5	day^{-1}
Observed first-order degradation rate in benthos	K_{Bs}	0 - 0.5	day^{-1}
Bacterial activity or concentration of bacterial agent	P_{bac}	10^2 - 10^7	cells/mL
Observed second-order rate coefficients for chemical in water and benthos	k_{Bwj} k_{Bsj}	0 - 10^{-6}	mL/cell-day
Biodegradation temperature coefficients for chemical in phase j in water and benthos	Q_{Twj} Q_{Tsj}	1.5 - 2.5	
Water temperature	T	4 - 30	°C

where: K_{Bw} = net biodegradation rate constant in water segment, day^{-1}

K_{Bs} = net biodegradation rate constant in sediment (benthic) segment, day^{-1}

k_{Bwj} = second-order biodegradation rate constant for chemical in phase j in water segments, ml/cell-day

k_{Bsj} = second-order biodegradation rate constant for chemical in phase j in benthic segments, mL/cell-day

$P_{bac}(t)$ = active bacterial population density in segment, cell/ml

f_j = fraction of chemical in phase j

IPX biodegradation data specifications are summarized in Table 1.12. The second-order rate constants for water and for sediment segments can be specified as constants. Temperature correction factors can be zero. If non-zero temperature correction factors are specified, IPX can modify each rate constant k_B as follows:

$$k_{Bwj}(T) = k_{Bwj} Q_{Twj}^{(T-20)/10} \tag{1.83}$$

$$k_{Bsj}(T) = k_{Bsj} Q_{Tsj}^{(T-20)/10} \tag{1.84}$$

where: Q_{Twj} = "Q-10" temperature correction factor for biodegradation of chemical in phase j in water

Table 1.13. Size of Typical Bacterial Populations in Natural Waters.

Water Body Type	Bacterial Numbers (cells/ml)	Reference
Oligotrophic Lake	50 - 300	a
Mesotrophic Lake	450 - 1,400	a
Eutrophic Lake	2000 - 12,000	a
Eutrophic Reservoir	1000 - 58,000	a
Dystrophic Lake	400 - 2,300	a
Lake Surficial Sediments	8×10^9 - 5×10^{10} cells/100 g dry wt	a
40 Surface Waters	500 - 1×10^6	b
Stream Sediments	10^7 - 10^8 cells/100 g dry wt	c
Rur River (Winter)	3×10^4	d

a) Wetzel (1975); enumeration techniques unclear.
b) Paris et al. (1981); bacterial enumeration using plate counts.
c) Herbes & Schwall (1978); bacterial enumeration using plate counts.
d) Larson et al. (1981): bacterial enumeration using plate counts.

Q_{Tsj} = "Q-10" temperature correction factor for biodegradation of chemical in phase j in benthic segments
T = ambient temperature in segment, °C

The temperature correction factors represent the change in biodegradation rate constants resulting from a 10°C temperature increase. Values in the range of 1.5 to 2 are common.

Total bacterial populations for water and benthic segments are input using parameter BACTOG(ISEG). Typical population size ranges are given in Table 1.13. Time functions that multiply the water and benthic segment populations are input using functions BACNW and BACNS. The product of parameter BACTOG and these time functions gives a description of the time- and space-variation of bacterial populations. If the time functions are omitted, populations remain constant in time.

Environmental factors other than temperature and population size can limit bacterial rates. Potential reduction factors must be considered externally by the user. Nutrient limitation can be important in oligotrophic environments. The following reduction factor was used by Ward and Brock (1976) to describe phosphate limitation of hydrocarbon degradation:

$$f_{PO_4} = \frac{0.0277 C_{PO_4}}{1 + 0.0277 C_{PO_4}} \tag{1.85}$$

where: C_{PO_4} = dissolved inorganic phosphorus concentration, µg/L

This adjustment must be made to the input rate constants by the user for situations of nutrient limitation. Low concentrations of dissolved oxygen can also cause reductions in biodegradation rates. Below DO concentrations of about 1 mg/L, rates decrease. When anoxic conditions prevail, most organic substances biodegrade more slowly. Because biodegradation reactions are generally more difficult to predict than physical and chemical reactions, site-specific calibration may be important.

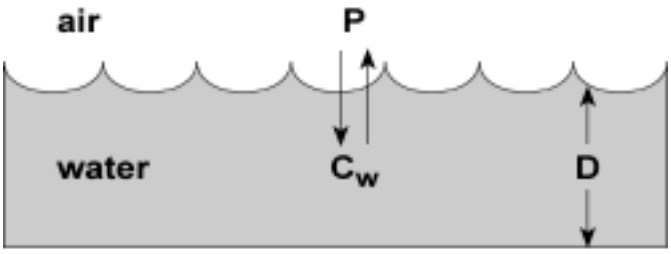
1.6.7 Volatilization

Volatilization is the gradient-driven movement of a chemical across the air-water interface. Other mass transfer processes between the air and water (dry and wet particle deposition and rain dissolution) are treated as loads in IPX. The dissolved chemical attempts to equilibrate with the gas phase partial pressure, as illustrated in Figure 1.10. The equation in this figure shows that equilibrium occurs when the dissolved concentration equals the partial pressure divided by Henry's Law Constant. Volatile organic chemical concentrations in the atmosphere are often much lower than partial pressures equilibrated with water concentrations. In such cases, volatilization reduces to a first-order process with a rate proportional to the conductivity and surface area divided by volume:

$$K_v = k_v \frac{A_s}{V} f_d = k_v \frac{f_d}{D} \tag{1.86}$$

where: K_v = net volatilization rate constant, day^{-1}
k_v = conductivity of the chemical through water, m/day
A_s = surface area of water segment, m^2
V = volume of the water segment, m^3
D = average depth of the segment, m
f_d = dissolved fraction of the chemical

The value of k_v, the conductivity, depends on the intensity of turbulence in the water body and the overlying atmosphere. Mackay and Leinonen (1975) discussed conditions under which the value of k_v is primarily determined by the intensity of turbulence in the water. As the Henry's Law constant increases, the conductivity tends to be increasingly influenced by the



$$\frac{\partial C_w}{\partial t} = - \frac{k_v}{D} \left(Cw - \frac{C_a}{H/RT} \right)$$

C_w = dissolved concentration in water, µg/L

C_a = concentration in air, µg/L

H = Henry's law constant, atm/M

R = gas constant (8.206 x 10-5), atm/M-K

T = water temperature, K

D = depth, m

k_v = rate constant, m/day (conductivity)

Figure 1.10. Volatilization.

intensity of water turbulence. As the Henry's Law constant decreases, the conductivity tends to be increasingly influenced by the intensity of atmospheric turbulence.

Henry's Law constants generally increase with increasing vapor pressure and decrease with increasing solubility of a compound. Highly volatile, low solubility compounds are most likely to exhibit mass transfer limitations in the water (liquid phase resistance). Relatively nonvolatile, high solubility compounds are more likely to exhibit mass transfer limitations in the air (gas phase resistance). Volatilization rates are usually smaller in comparatively quiescent lakes and reservoirs than in relatively turbulent rivers and streams.

In cases where the volatilization rate is regulated by turbulence in the water phase, estimates of volatilization can be obtained from results of laboratory experiments. As discussed by Mill et al. (1982), small flasks containing a solution of a pesticide dissolved in water that have been stripped of oxygen can be shaken for specified periods of time. The amount of pollutant lost and oxygen gained through volatilization can be measured and the ratio of conductivities (KVOG) for pollutants and oxygen can be calculated. As shown by Tsivoglou and Wallace (1972), this ratio should be constant and independent of the turbulence in the water body. Therefore, if the reaeration coefficient for a receiving water body is known or estimated, and the ratio of the conductivity for the pollutant to the reaeration coefficient has been determined, the pollutant conductivity can be directly estimated.

In IPX, the dissolved concentration of a compound in a surface water column segment can volatilize at a rate determined by the two-layer resistance model (Whitman, 1923), where the conductivity is the reciprocal of the total resistance:

$$k_v = \left(R_L + R_G\right)^{-1} = \left(K_L^{-1} + K_G^{-1}\right)^{-1} \qquad (1.87)$$

where: R_L = liquid phase resistance, day/m
R_G = gas phase resistance, day/m
K_L = liquid phase transfer coefficient, m/day
K_G = gas phase transfer coefficient, m/day

The two-resistance model assumes that two “stagnant films” are bounded on either side by well mixed compartments. Concentration differences are the driving force for the water layer diffusion. Differences in partial pressures drive the diffusion for the air layer. At equilibrium, the same mass must pass through both films, and the resistances combine in series. Another resistance, the transport resistance between the two interfaces, is assumed to be negligible. However, this may not be true in two cases: very turbulent conditions and in the presence of surface active contaminants. Although this two-resistance method, the Whitman model, is rather simplified in its assumption of uniform layers, it has been shown to be as accurate as more complex models (for example, surface renewal and penetration theories). Laboratory studies of volatilization of organic chemicals confirm the validity of the method as an accurate predictive tool (Burns et al. 1982).

IPX allows the user considerable flexibility in specification of the volatilization rate. The volatilization rate may be input directly or calculated from a combination of semi-theoretical

relationships for the liquid and gas phase mass transfer rates, K_L and K_G, that follow. These options are selected by specification of the constants XKL and XKG.

Several formulations are available for computing liquid phase mass transfer rates. For segments with depths less than 0.61 m the Owens formula can be used to calculate an oxygen reaeration rate, which is then converted to a chemical-specific liquid phase mass transfer rate:

$$K_L = 5.349 \frac{u^{0.67}}{D^{0.85}} \left(\frac{MW_{O2}}{MW_C} \right)^{0.5} \tag{1.88}$$

where: u = velocity of the water, m/s
D = segment depth, m
MW_{O_2} = molecular weight of diatomic oxygen, g/mole = 32.
MW_C = molecular weight of chemical, g/mole

For segments where the velocity is less than 0.52 m/s or the depth is greater than 13.584 $u^{2.9135}$ (m), a modified form of the O'Connor-Dobbins formulation can be used to compute a chemical-specific liquid phase mass transfer rate:

$$K_L = \left(\frac{D_{wO2}}{D} \right)^{0.5} \left(\frac{MW_{O2}}{MW_C} \right)^{0.5} 8.64 \text{x} 10^4 \tag{1.89}$$

where: D_{wO_2} = diffusivity of oxygen in water, cm^2/s

For other cases, the Churchill formulation can be used to calculate a liquid phase mass transfer rate:

$$K_L = 5.049 \frac{u^{0.969}}{D^{0.673}} \left(\frac{MW_{O2}}{MW_C} \right)^{0.5} \tag{1.90}$$

For cases where mass transfer is controlled by the wind velocity, typical of lakes and reservoirs, formulations presented by O'Connor (1983b) and Mackay and Paterson (1986) can be used. Two forms of the O'Connor liquid phase mass transfer formulation are available. The O'Connor "short" form, which is applicable for hydrodynamically-smooth (viscous) conditions is:

$$K_L = \left[u_* \left(\frac{\rho_a}{\rho_w} \right)^{0.5} \frac{\kappa^{0.33}}{\lambda_2} Sc_w^{-0.67} \right] 8.64 \text{x} 10^4 \qquad (1.91)$$

where: u_* = shear velocity = $C_d^{0.5}$ W_{10}, m/s

C_d = coefficient of drag = 0.0011

W_{10} = wind velocity 10 m above water surface, m/s

ρ_a, ρ_w = density of air and water, g/m^3

κ = von Kármán constant = 0.4

λ_2 = dimensionless viscous sublayer thickness = 4

Sc_w = Schmidt Numbers for water = $\frac{\nu_w}{D_w}$

D_w = diffusivity of chemical in water, cm^2/s

ν_w = viscosity of water, cm^2/sec

The O'Connor "long" form adds a second term to Equation 1.91 to account for turbulence-induced surface renewal at the boundary of the diffusional sublayer:

$$\frac{1}{K_L} = \frac{8.64 \text{x} 10^4}{\left[u_{*oL} \left(\frac{\rho_a}{\rho_w} \right)^{0.5} \frac{\kappa^{0.33}}{\Gamma(u_{*oL})} Sc_w^{-0.67} \right]} + \frac{8.64 \text{x} 10^4}{\left[\left(\frac{\rho_a \nu_a}{\rho_w \nu_w} \right) \frac{D_w u_{*oL}}{\kappa Z_0(u_{*oL})} Sc_w^{-0.67} \right]^{0.5}} \qquad (1.92)$$

where: u_{*oL} = shear velocity, cm/s (defined in Equation 1.95)

$\Gamma(u_{*oL})$ = dimensionless sublayer thickness

$$= \Gamma \left(\frac{u_{*oL}}{u_{*oLC}} \right) e^{-\left(\frac{u_{*oL}}{u_{*oLC}} + 1 \right)}, \text{ for } u_{*oL} \geq u_{*oLC} \qquad (1.93)$$

$= \Gamma_0$, for u*oL < u*oLC

u_{*oLC} = critical shear velocity, cm/s = 11.0

Γ_0 = critical sublayer thickness = 5

$Z_0(u_{*oL})$ = roughness height, cm

$$\frac{1}{Z_0(u_{*oL})} = \frac{1}{Z_e} + \left[\frac{\lambda_1 u_{*oL}}{\nu_a} \right] e^{-\left(\frac{u_{*oL}}{u_{*oLt}} \right)} \qquad (1.94)$$

Z_e = limiting roughness length, cm = 0.35

λ_1 = 2.5

u_{*oLt} = transitional shear velocity, cm/s = 10

The shear velocity for this formulation is computed iteratively by successive substitution, using the relationship which expresses the drag coefficient (C_{doL}) in terms of the roughness height (Z_0):

$$u_{*oL} = \frac{\kappa W_{10}}{\ln\left(1000\left[\frac{1}{Z_e} + \left[\frac{\lambda_1 u_{*oL}}{\nu_a}\right] e^{-\left(\frac{u_{*oL}}{u_{*oLt}}\right)}\right]\right)} \qquad (1.95)$$

The values of the semi-empirical coefficients u_{*oLC}, Γ_0, Z_e, λ_1, and u_{*oLt} are those suggested by O'Connor to be applicable to large water bodies (oceans or large lakes).

The Mackay formulation is:

$$\begin{aligned} K_L &= \left[10^{-6} + 0.00341 u_{*m} Sc_w^{-0.5}\right] 8.64\text{x}10^4 && \text{for } u_{*m} > 0.3 \text{ m/s} \\ K_L &= \left[10^{-6} + 0.00144 u_{*m}^{2.2} Sc_w^{-0.5}\right] 8.64\text{x}10^4 && \text{for } u_{*m} \le 0.3 \text{ m/s} \end{aligned} \qquad (1.96)$$

where: u_{*m} = shear velocity, m/s = $0.01\ W_{10}\ (6.1 + 0.63\ W_{10})^{0.5}$

If the rate of oxygen reaeration for the water body is known (for instance, if reaeration studies have been conducted for dissolved oxygen modeling), then a chemical-specific liquid phase mass transfer rate may be calculated as:

$$K_L = K_{LO_2} k_{vo} = K_{LO_2} \left(\frac{MW_{O_2}}{MW_C}\right)^{0.5} \qquad (1.97)$$

where: K_{LO_2} = oxygen reaeration rate, m/day

k_{vo} = ratio of chemical volatilization to reaeration conductivities

This rate can be modified in space and time through proper specification of model segment parameters and time functions for reaeration.

Several formulations are also available for computing gas phase mass transfer rates. The O'Connor-Rathbun formulation can be used to compute a chemical-specific gas transfer rate (O'Connor, 1983a; Rathbun, 1990):

$$K_G = \left[0.001\left(\frac{1}{Sc_a}\right)^{0.667} W_{10}\right] 8.64\text{x}10^4 \qquad (1.98)$$

where: Sc_a = Schmidt Number for air = $\frac{\nu_a}{D_a}$

D_a = diffusivity of chemical in air, cm^2/s

ν_a = kinematic viscosity of air, cm^2/s

Mill et al. (1982) found that the gas phase mass transfer rate for a chemical can be estimated from the evaporation rate of water:

$$K_G = 168\left(\frac{MW_W}{MW_C}\right)^{0.25} W_{10} \tag{1.99}$$

where: MW_W = molecular weight of water, g/mole = 18

The O'Connor gas phase mass transfer formulation (O'Connor, 1983b) is:

$$K_G = \left[u_{*os}\frac{\kappa^{0.33}}{\lambda_2} Sc_a^{-0.666}\right] 8.64\text{x}10^4 \tag{1.100}$$

The Mackay gas phase mass transfer formulation (Mackay and Paterson, 1985) is:

$$K_G = \left\lfloor u_{*m} 0.0462 Sc_a^{-666} + 10^{-3}\right\rfloor 8.64\text{x}10^4 \tag{1.101}$$

For flowing systems, Ambrose et al. (1988) assume that the gas phase mass transfer rate is constant at 100 m/day. As wind speeds decrease, mass transfer rates in the gas phase also decrease. Under still-air conditions, Mackay and Leinonen (1975) suggested that K_G is 86.4 m/day (0.001 m/s), representing a minimum rate of gas phase mass transfer. The user has the option of specifying gas phase mass transfer rates below this value, however.

Chemical diffusivities in air (D_a) and water (D_w) are calculated internally by IPX. At a minimum, the chemical molecular weight must be input to allow calculation of diffusivities. If the LeBas molar volume (V_b) is also input, then diffusivities will be calculated as functions of temperature. The calculation of V_b based upon molecular structure, is presented in Lyman et al. (1982).

The Henry's Law constant, HLC or H, of a chemical is defined as the ratio of the vapor pressure, P_v to solubility, S:

$$H = MW_C\left(\frac{P_v}{S}\right) \tag{1.102}$$

where: H = Henry's Law constant (HLC), atm m^3/mol
P_V = vapor pressure, atm
S = solubility, mg/L

The Henry's Law constant for a chemical may be input directly, or calculated from vapor pressure and solubility data. Mackay and Shiu (1981) and Schnoor et al. (1987) provide extensive reviews of available HLC data.

Henry's Law constants vary with water temperature. IPX provides several options to handle this temperature dependence. For many chemicals, the HLC can be directly expressed as a function of temperature in the following form:

$$\ln H = a_0 - \frac{a_1}{T + 273.15} \tag{1.103}$$

where: a_0, a_1 = user input HLC temperature function factors
T = water temperature, °C

For example, the Henry's Law constants for polychlorinated biphenyls (PCBs) (Tateya et al. 1988) and mirex (Yin and Hassett, 1986) expressed as functions of temperature are:

PCBs: $$\ln H = 18.53 - \frac{7868}{T + 273.15}$$

mirex: $$\ln H = 29.27 - \frac{10849}{T + 273.15}$$

Alternatively, Henry's Law constant may be input as a chemical constant, or calculated by IPX according to Equation 1.102. For chemicals which are solids at ambient temperature, calculations of Henry's Law constant using Equation 1.102 require subcooled liquid vapor pressure and solubility. IPX can convert solid-phase input of P_v and S to subcooled liquid values, using an algorithm described by McLachlan and Mackay (1987). This conversion is only performed if the melting temperature is below ambient temperature. The conversion from solid (P_S) to subcooled liquid vapor pressure (P_L) is:

$$\ln\left(\frac{P_S}{P_L}\right) = -\frac{\Delta s}{R}\left[\frac{T_M}{T} - 1\right] \quad (1.104)$$

where: Δs = Entropy of fusion, 56 J/mol K
R = Gas constant, 8.314 J/mol K
T_M = Melting temperature, K
T = Temperature at which P_S is valid, K

P_L is then corrected for water temperature using the Kistiakowski Linear Enthalpy equation:

$$\ln\left(\frac{P_L}{P_B}\right) = -(4.4 + \ln T_B)\left[1.803\left(\frac{T_B}{T} - 1\right) - 0.803\ln\left(\frac{T_B}{T}\right)\right] \quad (1.105)$$

where: P_L = Subcooled liquid vapor pressure at temperature T
P_B = Vapor pressure at boiling point (1 atm)
T_B = Boiling temperature (K) at 1 atm
T = Water temperature (K)

Iterative solution of Equation 1.105 is performed to calculate the chemical's boiling temperature using the subcooled liquid vapor pressure and its reference temperature (assumed to be 293.15 K). Then, P_L is adjusted for temperature using Equation 1.105, and HLC is calculated using Equation 1.102. Solubility is not corrected for temperature, because S is nearly constant over the range of 0 to 25˚C (at least in comparison to the variation in vapor pressure).

Alternatively, if the overall volatilization rate is computed for a temperature of 20°C, this rate can be adjusted for temperature as follows:

$$k_v(T) = k_{v20}\theta^{T-20} \quad (1.106)$$

where: θ = user-specified temperature correction factor
T = water temperature, °C

This would be an appropriate option if HLC was input as a chemical constant.

Although many calculations may be necessary to compute chemical volatilization rates, most are performed internally and require users to specify relatively few parameters. The number of constants required depends on the options selected. For example, if the Henry's Law constant

Table 1.14. IPX volatilization data.

Description	Notation	Range	Units
Measured or calibrated conductance	k_v	0 - 25	m/day
Henry's Law Constant	H	10^{-7} - 10^{-1}	$\frac{atm\,m^3}{mol}$
Vapor pressure	P_v		atm
Solubility	S		mg/L
LeBas molar volume	V_b		cm^3/mol
Melting temperature	T_M		°C
Concentration of chemical in the atmosphere	C_a	0 - 1000	µg/l
Molecular weight of chemical	MW_C	10 - 10^3	g/mol
Oxygen Reaeration coefficient	K_{LO_2}	0.6 - 25	m/day
Experimentally measured ratio of volatilization to reaeration	k_{vo}	0 - 1	
Current velocity	u	0 - 2	m/sec
Water depth	D		m
Water temperature	T	4 - 30	°C
Wind speed 10 m above water surface	W_{10}	0 - 20	m/sec

for a solid-phase chemical is calculated internally from vapor pressure and solubility, then melting temperature becomes a required input. If k_{vo} is not measured, it will be calculated internally from molecular weight. IPX volatilization data specifications are summarized in Table 1.14.

1.6.8 Extra Reaction

IPX allows the user to specify an additional second-order reaction for the various phases of each chemical:

$$K_E = [E]\sum_j k_{ej} f_j \qquad (1.107)$$

where: K_E = net extra reaction rate constant, day^{-1}

[E] = intensity of environmental property driving the reaction

k_{ej} = second-order rate constant for chemical in phase j, $[E]^{-1}$ day^{-1}

f_j = fraction of chemical in phase j

An example of a kinetic process that may be modeled by this extra reaction is reduction. For a reduction reaction, [E] may be interpreted as the concentration of environmental reducing agents RH_2, so that:

$$C + RH_2 \Rightarrow P \tag{1.108}$$

where: C = concentration of chemical C, mole/L
RH_2 = concentration of RH_2, (= [E]) moles/L
P = reduced product, moles/L

The reducing agent and the second-order rate constant must be identified and quantified by laboratory kinetics studies. If both the environmental oxidizing and reducing agents are in excess, then two chemicals may be simulated as a redox pair:

$$C_1 + RO_2 \Leftrightarrow C_2 + RH_2 \tag{1.109}$$

where: C_1 = reduced chemical
C_2 = oxidized chemical
RO_2 = oxidizing agent
RH_2 = reducing agent

Laboratory kinetics studies can control the concentrations of RO_2 and RH_2 to determine rate constants for both oxidation and reduction. These may be specified as constants k_o (for oxidation) and k_E (for the "extra" reaction). In this example, since there is interconversion between the two chemicals being simulated, yield coefficients must also be specified. The spatially variable concentrations [RO_2] and [RH_2] must be specified as parameters.

1.7 SIMULATING THE TRANSPORT AND FATE OF HEAVY METALS USING IPX

Although designed explicitly for organic chemicals, IPX can be used to simulate metals with judicious specification of model parameters. Heavy metals in the aquatic environment can form soluble complexes with organic and inorganic ligands, sorb/bind with organic and inorganic particulates, and precipitate or dissolve. Because of the inherent complexity of metals behavior, site-specific calibration is required.

Although IPX does not compute ionic speciation, geochemical models such as MINTEQA1 (Brown et al. 1987) can be used to predict metal speciation for a given set of

environmental conditions. These calculations can be used to parameterize an IPX simulation. All soluble complexes with the free ion are summed to give the dissolved metal concentration. Precipitated metal phased can be lumped with all sorbed phases to give particulate "sorbed" metal concentration. A spatially variable lumped partition coefficient K_p describes the two phases. There is no general consistency in reported K_p values for particular metals in the natural environment, so site-specific values will likely be necessary. Partition coefficients may depend upon the sorbent character, including mineralogy, chemical structure, composition and electrical-chemical properties, presence of coatings, and the age and origin of humic substances. Table 1.15 summarizes K_p values reported in Delos et al. (1984) for eight metals. These values are generally high, and are provided as a starting point for simulation. Spatially-variable K_p values can be input to IPX using the parameter FOC(ISEG,I) and omitting all other partitioning parameters.

1.8 SIMULATION COMPLEXITY LEVELS

The chemical transport and fate processes in IPX can be implemented at various levels of complexity. These different levels involve increasing sophistication in solids behavior, equilibrium partitioning, and kinetic reactions. Solids behavior may be modeled at four levels of complexity: 1. descriptive solids concentration field, 2. descriptive solids concentration field with specified solids transport rates, 3. simulated total solids, and 4. three simulated solids types. Equilibrium partitioning may be modeled at five levels of complexity: 1. constant partition coefficient, 2. spatially variable partition coefficients, 3. hydrophobic sorption, and 4. solids-dependent partitioning. Kinetic reactions may be modeled at four levels of complexity: 1. constant half-life or rate constants, 2. spatially variable rate constants, 3. second-order rates, and 4. second-order rates with transformation products. Each complexity level is discussed in detail in the following section.

The increasing complexity levels permit more realistic description and extrapolation of the solids, equilibrium, and kinetic processes. However, more complex representations of processes generally require that users specify more model parameters. Although quicker and easier to construct simulations for lower complexity, the corresponding decrease of model capabilities requires more judgment on the part of the user. For example, consider analyzing a problem where the dissolved phase of a transformation product is extremely toxic. Useful simulations of this problem at a low complexity level would be difficult. For best results, the user must match the complexity of the simulation with the requirements of the problem.

Table 1.15. Speciation of priority metals between dissolved and particulate phases as a function of suspended solids concentrations in streams.

Metal	SS (mg/L)	K_p (L/kg)	% Dissolved	% Particulate
Arsenic	1	5×10^5	70	30
	10	9×10^4	50	50
	100	2×10^4	30	70
	1000	3×10^3	24	76
Cadmium	1	4×10^6	20	80
	10	3×10^5	25	75
	100	2×10^4	30	30
	1000	2×10^3	40	60
Chromium	1	3×10^6	25	75
	10	4×10^5	20	80
	100	5×10^4	17	83
	1000	5×10^3	15	85
Copper	1	1×10^6	50	50
	10	2×10^5	30	70
	100	3×10^4	25	75
	1000	6×10^3	14	86
Lead	1	3×10^5	75	25
	10	2×10^5	30	70
	100	1×10^5	10	90
	1000	9×10^4	1	99
Mercury	1	3×10^6	25	75
	10	2×10^5	30	70
	100	2×10^4	30	70
	1000	1×10^3	45	55
Nickel	1	5×10^5	70	30
	10	1×10^5	50	50
	100	4×10^4	20	80
	1000	9×10^3	10	90
Zinc	1	1×10^6	40	60
	10	2×10^5	30	70
	100	5×10^4	17	83
	1000	1×10^4	10	90

As each simulation complexity level is described, specific IPX input variable names and options are mentioned. Users should refer to Chapter 2 for more detailed explanations.

1.8.1 Simulating Solids

Level 1--The simplest description of solids is to specify an average solids concentration field. This is accomplished by setting the initial conditions for system 1 to observed concentrations and setting SYSBY(1), SYSBY(2), and SYSBY(3) to 1. It is not necessary to specify settling and resuspension velocities. Concentrations of the specified solids will remain constant but will influence chemical partitioning and, indirectly, transport and transformation. Particulate phase chemicals will not settle or resuspend.

Level 2--The next level for solids is to specify an average concentration field for a single solids type along with settling, resuspension velocities. As before, initial conditions for system 1 are specified as average solids concentrations and SYSBY(1), SYSBY(2), and SYSBY(3) set to 1. Solids transport velocities are specified in transport fields 3 and 6. Solids concentrations remain constant but will directly influence chemical partitioning; solids transport velocities will allow particulate chemical transport between the water column and sediments.

Level 3--The third level for solids is to simulate total solids. Loads, boundary concentrations, and initial conditions are specified for system 1. Settling and resuspension velocities are specified in transport fields 3 and 6. Solids concentrations can be calibrated to observed data, leading to more accurate calculations of particulate chemical transport. Particulate chemicals are transported between water and sediments.

Level 4--The fourth level for solids is to simulate multiple sediment types. Loads, boundary concentrations, and initial conditions are specified for systems 2, 3, and 4. Solids settling and resuspension velocities are specified in transport fields 3-6. Concentrations of each solids type can be independently calibrated to observed data, leading to more accurate calculations of solids transport, chemical partitioning, and chemical transport.

1.8.2 Simulating Equilibrium Partitioning

Level 1--The simplest equilibrium partitioning is described by a single, constant partition coefficient. This is done by specifying a value for PIXC(1,1) and omitting all other partitioning information such as LKOW, LKOC, and FOC(ISEG,1). Although the partition coefficient is constant, the dissolved and sorbed chemical fractions vary with solids concentrations:

$$f_d = \frac{1}{1 + K_p M_1 / n} \tag{1.110}$$

$$f_p = \frac{K_p M_1 / n}{1 + K_p M_1 / n} = 1 - f_d \tag{1.111}$$

where: K_p = partition coefficient, L/kg
M_1 = solids concentration, kg/L
n = porosity

Porosity is calculated internally in IPX from input sediment density and solids concentration:

$$n = 1 - \frac{M_1}{DSED(1)} \tag{1.112}$$

where: DSED(1) = sediment density of solids type 1, specified under initial conditions, kg/L

Level 2--The next level for equilibrium partitioning is to specify spatially-variable partition coefficients. This is done by specifying K_p values with the parameter FOC(ISEG,1) and omitting all other partitioning information such as LKOW, LKOC, and PIXC(1,1). The equations used by IPX are as described for Equilibrium Level 1. This option allows improved site-specific calibration of partition coefficients to observed ratios between dissolved and particulate chemical concentrations.

Level 3--The third level of complexity for equilibrium partitioning is spatially-variable K_p values for hydrophobic sorption. This is done by specifying values for FOC(1,ISEG) and LKOC or LKOW. If values for DOC(ISEG) are specified, then IPX will also calculate binding to dissolved organic carbon. If concentrations for sediment types 2 and 3 are specified or simulated along with corresponding FOC(2,ISEG) and FOC(3,ISEG) values, then IPX will calculate the fraction of chemical in five phases:

$$K_{pj}(x) = K_{oc} f_{ocj}(x) \qquad \text{j = 1, 2, 3} \tag{1.113}$$

$$f_d = \frac{1}{1 + \sum K_{pj} M_j / n + K_{oc} DOC / n} \qquad \text{j = 1, 2, 3} \tag{1.114}$$

$$f_p = \frac{\sum K_{pj} M_j / n}{1 + \sum K_{pj} M_j / n + K_{oc} DOC / n} \qquad j = 1, 2, 3 \qquad (1.115)$$

$$f_b = \frac{K_{oc} DOC / n}{1 + \sum K_{pj} M_j / n + K_{oc} DOC / n} \qquad j = 1, 2, 3 \qquad (1.116)$$

This level allows improved description of chemical partitioning, binding, and transport as well as improved description of hydrophobic sorption for different sediment regimes.

Level 4--The next level of complexity adds solids-dependent partitioning to hydrophobic sorption. This is done by specifying values for NUX(1) (ν_x), the solids-dependent partitioning constant. IPX calculates the partition coefficient as:

$$K_p = \frac{K_{po}}{1 + K_{oc} \sum f_{ocj} M_j / \nu_x} = \frac{K_{oc} \sum f_{ocj}}{1 + K_{oc} \sum f_{ocj} M_j / \nu_x} \qquad (1.117)$$

where: K_p = the solids dependent partition coefficient, L/kg
K_{po} = the solids independent partition constant, L/kg

If no values are specified for NUX(1) (ν_x), then TOXI4 assigns a large default value (i.e. no particle effect). A value of between 1 to 10 is representative of many surface waters. However, solids-dependent partitioning is not applied to sediment bed segments.

1.8.3 Simulating Kinetic Reactions

Level 1--The simplest kinetic reaction is described by a constant half-life or rate constant. If the user supplies first-order decay constants KV, KBW, KBS, KHN, KHH, KHOH, KO, KF, or KE for the transformation reactions, then they will be used directly:

$$S_{kl} = -\sum K_i C \qquad (1.118)$$

where: C = chemical concentration, mg/L
K_i = first-order decay constants, day^{-1}, including:
K_{HN} = neutral hydrolysis constant, day^{-1}
K_{HH} = acid-catalyzed hydrolysis constant, day^{-1}
K_{HOH} = base-catalyzed hydrolysis constant, day^{-1}
K_{Bw}, K_{Bs} = biodegradation constants for the water column and sediments, day^{-1}

K_F = photolysis constant, day^{-1}
K_O = oxidation constant, day^{-1}
K_V = volatilization constant, day^{-1}
K_E = extra reaction constant, day^{-1}

As an alternative, half-life may be are specified for any transformation process. If half-life is specified for the transformation reactions, it is internally converted to first-order rate constants:

$$K_i = \frac{0.693}{T_{Hi}} \tag{1.119}$$

where: T_{Hi} = half-life, days, including:
T_{HHN} = neutral hydrolysis half-life, days
T_{HHH} = acid-catalyzed hydrolysis half-life, days
T_{HOH} = base-catalyzed hydrolysis half-life, days
T_{HBw}, T_{HBs} = biodegradation half-life for the water column and sediments, day^{-1}
T_{HF} = photolysis half-life, days
T_{HO} = oxidation half-life, days
T_{HV} = volatilization half-life, days
T_{HE} = extra reaction half-life, days

The converted half-life rate constants are then used as described by Equation 1.118.

Level 2--Because environmental conditions may change throughout a water body, decay rates are expected to vary. The second kinetic level allows spatially variable decay rate constants TOTKG(ICHM, ISEG) to be specified by the user so that:

$$S_{kC} = -K_{Tc}(x)C \tag{1.120}$$

where: $K_{Tc}(x)$ = spatially variable lumped first-order decay rate constant for chemical c, $days^{-1}$

For segments where a non-zero K_T is supplied for a chemical, IPX uses this value and bypasses further kinetic calculations. For those segments where K_T is zero or not specified, IPX will apply any specified process rate constants.

Level 3--Because environmental conditions may vary temporally as well as spatially, empirically-determined lumped decay-rate constants may be inappropriate when extrapolated. The third level of kinetic complexity calculates decay rates based on second-order kinetics so that:

$$-K_{Tc}(x,t) = -\sum_{j}\sum_{k} k_{jkc}(x,t)[E]_k f_{jc} \qquad (1.121)$$

where: K_{Tc} = overall first-order rate constant for chemical c, day^{-1}
k_{jkc} = second-order rate coefficient for phase j, process k of chemical c
$[E]_k$ = intensity of environmental property affecting process k
f_{jc} = fraction of chemical c in phase j

Users may implement any given reaction by specifying values for the rate constants (by phase), relevant environmental parameters, and time functions.

Level 4--The fourth level of kinetic complexity allows simulation of transformation products. This level is implemented by simulating two or more chemicals (NOSYS > 4) that react and interconvert by specifying appropriate yield coefficients for each process:

$$S_{kc_nc_m} = -\sum_{c_m}\sum_{k} K_{kc_m} C_{c_m} Y_{kc_nc_m} \qquad \text{for n = 4,NOSYS, n} \neq \text{m} \qquad (1.122)$$

$$\vdots \qquad\qquad \vdots$$

$$S_{kc_nc_m} = -\sum_{c_{nn}}\sum_{k} K_{kc_n} C_{c_n} Y_{kc_mc_n} \qquad \text{for m = 4, NOSYS, m} \neq \text{n} \qquad (1.123)$$

where: $S_{kc_nc_m}$ = production rate of chemical c_n from chemical c_m undergoing reaction k, mg/L-day
$S_{kc_mc_n}$ = production rate of chemical c_m from chemical c_n undergoing reaction k, mg/L-day
K_{kc_n} = effective rate coefficient for chemical c_n, process k, day^{-1}
K_{kc_m} = effective rate coefficient for chemical c_m, process k, day^{-1}
$Y_{kc_nc_m}$ = yield coefficients for production of chemicals c_n from chemical c_m undergoing reaction k, gm c_n/gm c_m
$Y_{kc_mc_n}$ = yield coefficients for production of chemicals c_m from chemical c_n undergoing reaction k, gm c_m/gm c_n

Yield constants can be specified for every possible combination of reactant chemicals, product chemicals, and reaction pathways.

1.9 SUMMARY OF DATA REQUIREMENTS

Chemical partitioning and transformation pathways add detail to the general mass equations presented in Section 1.2. However, these additional processes require specification of the environmental parameters, chemical constants, and environmental time functions as discussed in the preceding sections. This section provides a summary of data requirements.

The environmental data required for a chemical simulation depend upon which transformation processes are important. Table 1.16 lists the environmental properties influencing each process in IPX, and a range of expected values. For a series of simulations involving many compounds, approximate values for all environmental properties should be specified. For those processes found to be most important, better estimates of the relevant environmental properties can be provided in a second round of simulations.

The chemical properties of each compound control which transformation processes are important in a particular environment. Table 1.17 summarizes chemical properties influencing each process in IPX. Although the model allows specification of different rates for the dissolved, particulate, and DOC-bound chemical phases, such data are not generally available. Measured rate constants are often assigned to the dissolved chemical phase. The model also allows specification of temperature correction parameters for each process. Such data are often difficult to find without special studies, and need not be input except for very hot or cold conditions, or where seasonal variability is being studied.

Time variable functions can be used to study diurnal or seasonal effects on pollutant behavior. The 21 environmental time functions are summarized in Table 1.18. As shown, some of these time functions are multiplied by spatially variable parameters within TOXI4 to simulate environmental conditions that vary in time and space. If no temporal variability is required, time functions may be omitted. Default values for time functions is 1.0. However, unused functions can affect a simulation. For example, if left unspecified the default water temperature is 0 and all temperature-dependent reactions (such as volatilization) will be computed for 0°C (273.15 K).

Although the amount and variety of data potentially required for a simulation is large, actual data requirements for any particular simulation are generally small. Usually only sorption

Table 1.16. Environmental properties affecting interphase transport and transformation processes.

Environmental Property	Input Value	Environmental Process					
		K_p (1)	K_V (2)	K_H (3)	K_O (4)	K_F (5)	K_B (6)
Solids Concentrations:							
Suspended, mg/L	5 - 500	X					
Sediment Bed, kg/L	0.4 - 1.7	X					
Organic Carbon Fraction:							
Suspended Sediment	0.01 - 0.10	X					
Benthic Sediment	0.01 - 0.10	X					
Dissolved Organic Carbon, mg/L	0 - 10	X					
Water Column Depth, m	0.5 - 500		X				
Water Temperature, °C	4 - 30		X	X	X	X	X
Average Water Velocity, m/s	0 - 2		X				
Wind Speed at 10 m, in m/sec	0 - 20		X				
pH, Standard Units	5 - 9			X			
Concentration of Oxidants, moles/L	10^{-9} - 10^{-12}				X		
Surface Light Intensity, Langleys/day	300 - 700					X	
Cloud Cover, tenths of sky	0 - 10					X	
Light Extinction Coefficient, 1/m	0.1 - 5					X	
Active Bacterial Population:							
Suspended, cells/ml	10^3 - 10^6						X
Benthic, cells/100g	10^3 - 10^6						X

(1) Sorption; (2) Volatilization; (3) Hydrolysis; (4) Oxidation; (5) Photolysis; (6) Bacterial Degradation

Table 1.17. Chemical properties affecting interphase transport and transformation processes.

Chemical Property	Input Units	Environmental Process					
		K_p (1)	K_V (2)	K_H (2)	K_O (4)	K_F (5)	K_B (6)
Molecular Weight	g/mole		X				
LeBas molar volume	cm^3/mol		X				
Solubility	mg/L		X				
Vapor Pressure	atmospheres		X				
Melting temperature	˚C		X				
Octanol-Water Partition Coefficient	L_w/L_o	X					
Organic Carbon Partition Coefficient	L_w/kg_{oc}	X					
Henry's Law Constant	m^3-atm/mole		X				
Liquid Phase Volatilization/ Reaeration Ratio			X				
Alkaline Hydrolysis Rate Constant	L/mole-day		X				
Neutral Hydrolysis Rate Constant	day^{-1}			X			
Acid-Hydrolysis Rate Constant	L/mole-day		X				
Activation Energy for Alkaline, Neutral, and Acid Hydrolysis	kcal/mole		X				
Oxidation Rate Constant	L/mole-day			X			
Activation Energy for Oxidation	kcal/mole			X			
Depth-Integrated Photolysis Rate	m/day					X	
Measured Biodeg. Rate Constant	day^{-1}						X
Water Column Rate Constant	mL/cell-day						X
Benthic Rate Constant	mL/cell-day						X
Temperature Dependence Multiplier (for 10°C change)	-						X

(1) Sorption; (2) Volatilization; (3) Hydrolysis; (4) Oxidation; (5) Photolysis; (6) Bacterial Degradation

Table 1.18. Time variable environmental forcing functions (combinations of IPX time functions and constants/parameters).

Time Function		Constant or Parameter		Environmental Property
TEMPN(TMPFN)	x	TEMP(ISEG)	=	Water temperature (x,t), °C
VELN(VELFN)	x	VELOCG(ISEG)	=	Water velocity (x,t), m/sec
WINDN	x	WVEL(ISEG)	=	Wind speed at 10 m above the water surface (x,t), m/sec
PHNW	x	PH(ISEG)	=	Water column pH (x,t), *log* activity
PHNS	x	PH(ISEG)	=	Benthic pH (x,t), *log* activity
REARN	x	REAER(ISEG)	=	Reaeration or volatilization rate (x,t), m/day
AIRTMPN	x	AIRTMP	=	Air temperature (t), °C
CHLN	x	CHPHL(ISEG)	=	Chlorophyll concentration, mg/L
PHTON			=	Seasonal adjustment to light intensity (dimensionless)
BACNW	x	BAC(ISEG)	=	Water column bacteria population (x,t), cells/mL
BACNS	x	BAC(ISEG)	=	Sediment bacteria population (x,t), cells/mL

and one or two transformation processes will significantly affect a particular chemical. To simulate the transport of many soluble compounds in the water column, even sorption can often be disregarded. For empirical screening-level studies most environmental parameters, chemical constants, and time functions, can be ignored except the user-specified transformation rate constant TOTKG(ICHM,ISEG), the partition coefficient LKOC, and organic carbon fraction FOC(ISEG,J). Thus, IPX can be used as a first-order water pollutant modeling framework to conduct standard simulations of dye tracers, salinity intrusion, or coliform die-off. What is gained by the second-order process functions and resulting input data burden is the ability to extrapolate more confidently to future conditions. The user must determine the optimum amount of empirical calibration and process specification for each application.

1.10 SUMMARY OF MODEL EQUATIONS

The equations implemented in IPX account for the transport of dissolved and particulate materials in the water column and sediments as summarized below:

$$\frac{\Delta V_j}{\Delta t} = \sum_i \left(-Q_{ij}\right) + \left(P_j - E_j\right)A_j \qquad (1.124)$$

flow, precipitation, and evaporation

$$\frac{\Delta\left(V_j C_j\right)}{\Delta t} = \sum_i \left(-Q_{ij} C_{ij}\right) + \sum_i \left(-Q_{ij} C_{ij} f_{dj}\right)$$

water column and pore water advection

$$+ \sum_i \left(-R_{ij}\Delta C_{ij}\right) + \sum_i \left[-R_{pij}\left(\frac{C_{ij} f_{dj}}{n} - \frac{C_{ij} f_{di}}{n}\right)\right]$$

water column and pore water dispersion

$$+ \sum_i \sum_s \left(-w_{sij} A_{ij} C_j f_{psj}\right)$$

solids transport

$$+ \sum_L W_{Lj} + \sum_N W_{Nj} + \sum_B W_{Bj}$$

point, non-point, and boundary loads

$$+ \sum_k \sum_c \left(V_j S_{kcj}\right) \qquad (1.125)$$

kinetic transformations

where: j = segment index
i = adjacent segment index
s = solids transport field index
L = point source index
N = non-point source index
B = boundary source index
k = kinetic transformation index
c = chemical index
V_j = volume of segment j, m^3
C_j = concentration of the water quality constituent in segment j, g/m^3
t = time, day
E_j = evaporation rate from segment j, m/day
P_j = precipitation rate into segment j, m/day
A_j = surface area of segment j, m^2

Q_{ij} = advective flow between segments i and j, defined as positive when leaving segment j, and negative when entering, m^3/day

Q_{pij} = pore water flow between segments i and j, defined as positive when leaving segment j, and negative when entering j, m^3/day

C_{ij} = constituent concentration advected between i and j, g/m3

= $\omega C_j + (1 - n) C_i$ when entering j

= $\omega C_i + (1 - n) C_j$ when leaving j

ω = advection factor (numerical weighing factor), 0 - 0.5

W_{sij} = solids transport velocity between segments i and j, defined as positive when leaving segment j, and negative when entering, m/day

f_{dj} = dissolved fraction of chemical in segment j

f_{psj} = fraction of chemical sorbed to solid type s in segment j

R_{ij} = dispersive flow between segments i and j, m^3/day

$$= \frac{E_{ij} A_{ij}}{L_{cij}}$$

E_{ij} = dispersion coefficient between segments i and j, m^2/day

A_{ij} = cross-sectional area between segments i and j, m^2

L_{cij} = characteristic mixing length between segments i and j, m

R_{pij} = pore water diffusive exchange flow, m^3/day

$$= \frac{E_{ij} A_{ij}}{L_{cij}} \frac{n_{ij}}{\tau_{ij}}$$

τ_{ij} = average tortuosity of segments i and j, m water/m

n_{ij} = average porosity of segments i and j, m^3 water/m3

W_{Lj} = point source loads into segment j, g/day

W_{Nj} = non-point loads into segment j, g/day

Q_{j0} = boundary inflows to segment j, m^3/day

C_{Bj} = boundary concentrations for segment j, g/m^3

S_{kcj} = kinetic transformation k for chemical c within segment j, g/m^3-day

Water column advection and dispersion parameters are specified for transport between water column segments. Pore water advection and diffusion parameters are specified for transport between sediment segments as well as between adjacent water column and sediment segments. Sediment transport parameters representing settling and resuspension also link adjoining water column and sediment segments.

1.11 OTHER MODEL INPUTS

This section summarizes the model input parameters that must be specified in order to uniquely define and solve the mass balance equation and conduct a simulation. Detailed information regarding proper specification of all model inputs is presented in Chapter 2.

1.11.1 Model Identification and Control Parameters

These parameters identify the model input file. They include the number of water quality constituents simulated and the number of segments in the network. This group of parameters controls the simulation and checks the numerical stability of the solution. Simulation parameters include the initial and final times, integration time-steps, the advection factor, maximum concentrations, and a negative solution option. Also provided are text lines used to describe the water body simulated.

Initial simulation time, days--The time at the beginning of the simulation must be specified in order to synchronize all the time functions. The day, hour, and minute can be input. A simulation typically begins on day 1 (time-break zero).

Final simulation time, days--The desired time at the end of the simulation must be specified. The final time is input in fractional form (i.e. including decimal fraction, if any). For example, a one year simulation beginning on day one (time zero) would end at 365.0.

Integration time-step, days--A sequence of integration time-steps (Δt) must be specified, along with the time interval over which they apply. Given specific network and transport parameters, time-steps are constrained within a specific range to maintain stability and minimize numerical dispersion (solution inaccuracies). To maintain numerical stability, the advected, dispersed, and transformed mass of a segment at any time-step must be less than the resident mass of that segment at the beginning of the time-step. Mathematically, this can be expressed as:

$$\left(\sum QC_j + \sum R\Delta C_j + \sum SV_j\right)\Delta t < V_j C_j \qquad (1.126)$$

Rearranging Equation 1.118 to solve for Δt and applying the criterion over the entire network gives the maximum stable time-step size:

$$\Delta t_{max} = Min\left(\frac{V_j}{\sum_i Q_{ij} + \sum_i R_{ij} + \sum_k S_{jk}V_j / C_j}\right) \qquad (1.127)$$

If reactions are linear, the last term in the denominator reduces to ΣKV_j. However, most tributaries are advectively dominated and Δt will generally be controlled by advective flows.

Advection factor, dimensionless--IPX uses a finite difference approximation of the general mass balance differential equation (see Appendix A). The advection factor ω (described in Appendix A) is used to modify the finite difference approximation used by IPX. The value of this factor influences the stability of the solution at the expense of numerical accuracy (numerical dispersion). For ω = 0, a backward difference approximation is used. This approximation is the most stable and is recommended for most applications. However, the backward difference introduces the most numerical dispersion into the solution. For ω = 0.5, a central difference approximation is used. For ω = 1.0, a forward difference is used. However, as implemented in IPX, central and forward differences are numerically unstable and are not recommended.

The use of finite difference approximations in place of continuous spatial derivatives introduces numerical dispersion in the model solution. Numerical dispersion has the effect of an additional dispersive transport term on the numerical solution computed for the mass balance equation. If the advection factor ω = 0, a backward difference approximation of spatial derivative ($\partial C/\partial x$) is used for the advection term. The degree of numerical dispersion resulting from the backward difference approximation of the spatial derivative is:

$$E_{num} = \frac{uL}{2} \tag{1.128}$$

where: u = water (advective) velocity
L = length of the segment (Δx)

For the Euler numerical integration method (the solution method used in IPX), the forward difference approximation of the temporal derivative ($\partial C/\partial t$) is used. The degree of numerical dispersion resulting from the forward difference approximation of the temporal derivative is:

$$E_{num} = \frac{u^2 \Delta t}{2} \tag{1.129}$$

Therefore, the overall numerical dispersion resulting from the approximation of both the spatial and temporal derivatives is:

$$E_{num} = \frac{u}{2}(L - u\Delta t) \qquad (1.130)$$

Note that increasing the time-step to L/u (= Δx /u or V/Q) decreases numerical dispersion to zero. However, the conditions for numerical stability require a time-step somewhat less than V/Q for most segments. So, to maintain stability and minimize numerical dispersion in a water body subject to unsteady flow, the sequence of time-steps should be as large as possible, but always less than $\Delta t_{\max}$ given in Equation 1.127.

A non-zero advection factor is helpful in situations where the network size and time-step produce large numerical dispersion. A non-zero advection factor reduces the numerical dispersion produced by a particular velocity, length, and time-step combination. According to Bella and Grenney (1970):

$$E_{num} = \frac{u}{2}[(1 - 2\omega)L - u\Delta t] \qquad (1.131)$$

Note that a ω of 0 reduces this to Equation 1.130. Values of E_{num} for a segment length of 2000 meters and various combinations of velocities and time-steps are presented in Table 1.19. For a particular velocity, such as 0.4 m/sec, numerical dispersion can be reduced by increasing the time-step. For ω = 0, increasing the time-step from 1000 to 4000 seconds decreases E_{num} from 320 to 80 m^2/s. If the time-step must be 1000 seconds, however, numerical dispersion can still be reduced by increasing ω. In this case, increasing ω from 0 to 0.4 decreases E_{num} from 320 to 0 m^2/s.

Negative solution option--Normally, concentrations are not allowed to become negative. Unless the negative solution option is selected, if the concentration predicted at time $t + \Delta t$ is negative, IPX maintains a positive value by halving the concentration that was present at time t instead of allowing the value to become negative. The negative solution option lets the user bypass this procedure, allowing negative concentrations. This may be desirable for simulating dissolved oxygen deficit in the benthos, for example.

1.11.2 Boundary Parameters

Boundary concentrations, mg/L--Steady or time-variable concentrations must be specified for each water quality constituent at each boundary. A boundary is either a tributary inflow, a downstream outflow, or an open water end of the model network across which dispersive mixing

Table 1.19. Numerical Dispersion (m^2/s) values resulting from u and Δt for a Segment Length of L = 2000 m

	u (m/s)					
ω	0.1	0.2	0.4	0.6	0.8	1.0
	Δt = 1000 sec					
0.0	95	180	320	420	480	500
0.1	75	140	240	300	320	300
0.2	55	100	160	180	160	100
0.3	35	60	80	60	0	--
0.4	15	20	0	--	--	--
	Δt = 2000 sec					
0.0	90	160	240	240	160	0
0.1	70	120	160	120	0	--
0.2	50	80	80	0	--	--
0.3	30	40	0	--	--	--
0.4	10	0	--	--	--	--
	Δt = 4000 sec					
0.0	80	120	80	--	--	--
0.1	60	80	0	--	--	--
0.2	40	40	--	--	--	--
0.3	20	0	--	--	--	--
0.4	0	--	--	--	--	--
	Δt = 8000 sec					
0.0	60	40	--	--	--	--
0.1	40	0	--	--	--	--
0.2	20	--	--	--	--	--
0.3	0	--	--	--	--	--
0.4	--	--	--	--	--	--

can occur. Advective and dispersive flows across boundaries are specified by the transport parameters.

1.11.3 Point Source and Non-Point Source Loads

Point Source Loads, kg/day--Loads (external inputs) may be specified for each water quality constituent in any segment. Specified loads can steady or time-variable. These loads represent municipal and industrial wastewater discharges, urban and agricultural runoff, precipitation, and atmospheric deposition of pollutants, or any other external contaminant source.

1.11.4 Initial Conditions

Initial concentrations, mg/L--Concentrations of each constituent in each segment must be specified for the time at which the simulation begins. (Note: the concentrations specified will be used as the starting conditions for a simulation regardless of the start time specified.) For those water bodies with low transport rates, the initial concentrations of conservative substances may persist for a long period of time. Accurate simulation requires accurate specification of initial contaminant concentrations.

Dissolved fractions, dimensionless--The initial fraction of chemical dissolved in the water portion of a segment input as a fraction of total chemical concentration (0-1). The dissolved fraction is important in determining the mass of chemical transported by pore water flow and dispersion, and by solids transport. For simulation where equilibrium partitioning and binding are specified, dissolved fractions are computed from sorption parameters.

Solid densities, g/cm^3 --The density of each solid type. This is needed to compute the porosity of sediment bed segments. Porosity is a function of sediment concentration and the density of each solid type.

Maximum concentrations, mg/L--Maximum concentrations must be specified for each water quality constituent. The simulation is automatically aborted if a calculated concentration falls outside these limits. This usually arises from computational instability, and indicates the time-step must be reduced.

1.12 APPLYING THE MODEL

The first step when applying the model is to analyze the problem to be solved. What questions are being asked? How can a simulation model be used to address these questions? A water quality model can do three basic tasks: simulate present water quality conditions, provide generic predictions, and provide site-specific predictions. The first, descriptive task is to extend in some way a limited site-specific data base. Because monitoring is expensive, data seldom give the spatial and temporal resolution needed to fully characterize a water body. A simulation model can be used to interpolate between observed data; for example, locating the dissolved oxygen sag point in a river or the maximum salinity intrusion in an estuary. Of course such a model can be used to guide future monitoring efforts. Descriptive models also can be used to infer the important processes controlling present water quality. This information can be used to guide not only monitoring efforts, but also model development efforts.

Providing generic predictions is a second type of modeling task. Site-specific data may not be needed if the goal is to predict the types of water bodies at risk from a new chemical, or the critical conditions or risk (potential occurrence of event) for a particular contaminant exposure. A crude set of data may be adequate to screen a list of chemicals for potential risk to a particular water body. Generic predictions may sufficiently address the management problem to be solved (provided that the uncertainty of such predictions are explored and communicated with the results), or they may be a preliminary step in detailed site-specific analyses.

Providing site-specific predictions is the most stringent modeling task. Calibration to a good set of monitoring data is definitely needed to provide credible predictions. Because predictions often attempt to extrapolate beyond the present data base, however, the model also must have sufficient process integrity. Examples of this type of application include waste load allocation to protect water quality standards and feasibility analysis for remedial actions, such as tertiary treatment, phosphate bans, or agricultural best-management practices.

Analysis of the problem should dictate the spatial and temporal scales for the modeling analysis. Division of the water body into appropriately sized segments was discussed in Section 1.3. Users should extend the network upstream and downstream beyond the influence of the waste loads being studied to minimize the influence of uncertain boundary conditions. Users should also design the model network so that sampling stations and points of interest (such as water withdrawals) fall near the center (centroid) of a segment. Point source loads in streams and rivers with unidirectional flow should be located near the upper end of a segment. In estuaries and other water bodies with reversing flow, waste loads are best located near the centers of segments.

Once the model network is defined, a modeling study will proceed generally through four steps that involve, in some manner, hydrodynamics, mass transport, water quality transformations, and environmental toxicology. The first step addresses the issue of where water goes. This can be answered by a combination of gaging, special studies, and hydrodynamic modeling. Flow data or outputs from hydrodynamic models can be interpolated or extrapolated throughout the model network using the principle of continuity. The second step answers the question of where the material in the water is transported. This can be answered by a combination of tracer studies and model calibration. Dyes, salinity (conductivity), and heat are often used as tracers. The third step answers the question of how materials in the water and sediments are transformed and where they are ultimately transported. This is the main focus of many studies. Answers will generally depend on a combination of laboratory studies, field

monitoring, parameter estimation, calibration, and testing. The net result is sometimes called model validation or verification, which are elusive concepts. The success of this step depends on the skill of the user, who must combine specialized knowledge with common sense and skepticism into a methodical process. The final step answers the question of how this material is likely to affect target organisms, such as people or fish, or the ecological balance. Often, predicted concentrations are simply compared with water quality criteria adopted to protect the general aquatic community. Care must be taken to insure that the temporal and spatial scales assumed in developing the criteria are compatible with those predicted by the model. Sometimes principles of physical chemistry or pharmacokinetics are used to predict chemical body burdens and resulting biological effects.

CHAPTER 2

IPX INPUT DATA FILE STRUCTURE

2.1 IPX INPUT DATA FILE STRUCTURE OVERVIEW

The input required to run the IPX water quality modeling framework is divided into a series of data groups. The purpose of these data groups is to arrange all required model inputs into a consistent, logical structure. Each data group is used to enter model inputs related to a specific aspect of a simulation such as reaction kinetics and transport processes, etc. Data within a group are related to other data within the same group. An overview of each input file data group, A through K, is presented. Each data group is further divided into data records. Following this overview, the structure of each data group and its records are described in detail.

A - Model Identification and Simulation Control

Data Group A is used for model identification and specifying simulation control options. This data group requires specification of the number of segments and the number of systems. Numerical integration time-steps and print intervals for reporting simulation output are also specified.

B - Exchange (Dispersion) Coefficients

Data Group B is used to input dispersive exchanges for the water column and sediment pore water.

C - Volumes

Data Group C is used to input the volumes and hydraulic characteristics for each model segment.

D - Flows, Sediment Transport, and Precipitation/Evaporation

Data Group D is used to input water column flows, pore water flows, settling velocities, resuspension velocities, and precipitation/evaporation rates.

E - Boundary Concentrations

Data Group E is used to input the concentration of each state variable at the model boundaries. Boundary conditions must be specified for all state variables at each boundary.

F - Loads (Forcing Functions)

Data Group F is used to input loads (forcing functions) of each state variable to any model segment. Loads can be positive (source) or negative (sink) in magnitude and represent both point and non-point source inputs.

G - Environmental Parameters

Data Group G is used to input site-specific environmental characteristics of the modeled system that are constant temporally but can vary spatially (from segment to segment). A list of all parameters that may be included in a simulation are presented in Table 2.2.

H - Chemical Constants (Physicochemical Properties)

Data Group H is used to input the physicochemical properties of each state variable (solids type and chemical) simulated. Reaction yields for chemicals that transform from one modeled chemical to another modeled chemical are also specified. A list of all constants that may be included in a simulation are presented in Table 2.3-2.12.

I - Time Functions

Data Group I is used to input environmental characteristics of the modeled system that are constant spatially but can vary temporally. A list of all time functions that may be included in a simulation are presented in Table 2.13.

J - Initial Conditions

Data Group J is used to input initial concentrations (concentrations at the start time of the simulation) of each state variable in each model segment.

K - Surficial Sediment Age Layer Conditions

Data Group K is used to define surficial sediment aging characteristics and the initial distribution of sediment resuspension properties in each age layer for each surficial sediment segment in the model. The aging properties of all sediments in each age layer and the resuspension properties of freshly deposited sediments are also specified.

L - Initial Conditions for Deep Sediment Layers (Ghost Stack)

Data Group L is used to define initial conditions for deep sediment layers when the semi-Lagrangian sediment bed option is used. The physical configuration and physicochemical properties of each deep sediment layer (if any) in each sediment stack using the semi-Lagrangian bed option are specified.

2.2 IPX INPUT FILE DATA GROUP DESCRIPTIONS

2.2.1 Data Group A: Model Identification and Simulation Control

All parameters that define the number of state variables simulated, the number of model segments, time-step for numerical integration.

Record 1--Title of Simulation (A80)

HEADS = descriptive title of simulation (A80).

Record 2--Description of Simulation (A80)

TYPE = description of simulation (A80).

Record 3--Names of Variables Listed in Record 4 (A80)

HEADER = names of Record 4 variables, positioned properly; for user convenience only (A80).

Record 4--Simulation Control Parameters (8I5, 2F5.0, F3.0, F2.0, 3I5, F10.0)

KSIM = simulation type; 0 = dynamic. (I5)

Previous versions of the WASP4 framework from which IPX was derived allowed the user to chose either a dynamic or steady-state solution. However, IPX will only perform a dynamic mass balance so the value of **KSIM must always be 0**. This variable was left in the IPX code so users could use previously developed WASP4 input data files with a minimum of effort.

NOSEG = number of segments in model network. (I5)

NOSYS = number of model systems (state variables). (I5)

Systems 1-3 are solids and Systems 4-n are chemicals. If only one solids type is simulated with several chemicals, Systems 1, 2, or 3

could be used to simulate the single solids type while the two unused Systems would be "placeholders". Most IPX simulations will require that at least four systems be specified. For example, if a user wishes to simulate one chemical and one solid, the number of systems that must be specified is four: System 1 for all solids, Systems 2-3 would be "dummy" systems for which all computations should bypassed, and System 4 would be for the chemical.

ICFL = flag controlling use of restart file; 0 = neither read from nor write to restart file (initial conditions located in input file); 1 = write final simulation results to restart file (initial conditions located in input file); 2 = read initial conditions from restart file created by earlier simulation, and write final simulation results to new restart file. (I5) **(Option Not Available. Set ICFL = 0)**

MFLAG = flag controlling messages printed on screen during simulation; 0 = all messages printed; 1 = simulation time only printed; 2 = no messages printed. (I5)

JMASS = system number for which export computations will be performed. (I5)

IPX computes a detailed, segment by segment mass balance for all state variables (solids type or chemical) simulated. Export is defined as the sum of the mass transported by advection and dispersion across any model interface (internal or at a model boundary). In addition to computing export for the system (state variable) specified by JMASS, IPX automatically computes export for the sum all solids types simulated.

NEGSLN = negative solution option; 0 = prevents negative solutions; 1 = allows negative solutions. (I5)

The authors recommend that NEGSLN = 0 for all simulations. This option was originally developed to allow WASP4 users to simulate dissolved oxygen (DO) etc. where negative concentrations

represent DO deficit conditions. Code operation for NEGSLN = 1 has not been verified.

INTYP = time-step option; 0 = user inputs time-steps; 1 = model calculates time-step. (I5)

The authors recommend that INTYP = 0 and model time-steps be input by the user. Code operation for INTYP = 1 has not been verified.

ADFAC = advection factor; 0 = backward difference; 0.5 = central difference; [1 = forward difference but is unconditionally unstable;] 0 recommended. (F5.0)

ZDAY = day at beginning of simulation; 1 = first day. (F5.0)

ZHR = hour at the beginning of simulation. (F3.0)

MIN = minute at the beginning of simulation. (F2.0)

IDSY = system number for which results (concentrations) will be displayed on screen during simulation. (I5)

IDSG1 = "upstream" segment for which the mass export of JMASS will be computed and for which results (concentrations) will be displayed on screen. (I5)

IDSG2 = "downstream" segment for which the mass export of JMASS will be computed and for which results (concentrations) will be displayed on screen. (I5)

IDSG1 and IDSG2 define the model segment interface for which export computations will be performed. Export is computed as the sum of the mass transported across a model interface by advection and dispersion from IDSG1 to IDSG2. If the interface for which export is calculated is at a model boundary, one of the segments specified will be 0. Care must be taken to choose IDSG1 and IDSG2 such that the pair specifies a meaningful model interface. If

IDSG1 and IDSG2 do not define a model interface, all export computation will be spurious.

TADJ = factor by which input kinetic rates are adjusted; 0 or 1.0 will cause no adjustment; 24.0 will adjust rates input as hours^{-1} to days^{-1}; 86400.0 will adjust rates input as seconds^{-1} to days^{-1}. (F10.0)

Record 5--Time-Steps (I5, F5.0)

NOBRK = number of different model time-steps (I5)

TRST = frequency (time interval) in days at which output is written to the restart file; default value (if TRST is zero or not specified) = 5 days. (F5.0)

Record 6--Time-Steps (4(F10.0, F10.0)

SIMFVAL(I) = simulation time-step in days that will be used until the simulation time is greater than SIMFTIM(I). (F10.0)

SIMFTIM(I) = simulation time in days up to when time-step SIMFVAL(I) will be used. (F10.0)

where I = 1, NOBRK

Record 7--Number of Print Intervals for Reporting Output to *.dmp File and Option for Temporal Averaging (2I5)

NPRINT1 = number of print intervals for reporting output to *.dmp file. (I5)

VFLAG = option for reporting time averaged output to an additional file; 0 = instantaneous (point value) results to *.dmp file; 1 = time-averaged results reported to *.dma file (which is generated in addition to the *.dmp file). (I5)

Record 8--Print Intervals for Reporting Ouptput to *.dmp File (4(F10.0, F10.0))

PRINT1(I) = simulation results print interval in days that will be used until the simulation time is greater than TPRNT1(I). (F10.0)

TPRNT1(I) = simulation time in days up to when print interval PRINT(I) will be used. (F10.0)

where I = 1, NPRINT1

Record 9--Number of Print Intervals for Reporting Output to *.exp File (I5)

NPRINT2 = number of print intervals for reporting to *.exp file. (I5)

Record 10--Print Intervals for Reporting Output to *.exp File (4(F10.0, F10.0))

PRINT2(I) = simulation results print interval in days that will be used until the simulation time is greater than TPRNT2(I). (F10.0)

TPRNT2(I) = simulation time in days up to when print interval PRINT2(I) will be used. (F10.0)

where I = 1, NPRINT2

Record 11--Number of Print Intervals for Reporting Output to *.dma File (I5)

NPRINT3 = number of print intervals for reporting to *.dma file. (I5)

Record 12--Print Intervals for Reporting Output to *.dma File (4(F10.0, F10.0))

PRINT3(I) = simulation results print interval in days that will be used until the simulation time is greater than TPRNT3(I). (F10.0)

TPRNT3(I) = simulation time in days up to when print interval PRINT(I) will be used. (F10.0)

where I = 1, NPRINT3

Record 13--System Bypass Options (16I5)

SYSBY(ISYS) = bypass option for system ISYS; 0 = system will be simulated; 1 = system will be bypassed. (I5)

where ISYS = 1, NOSYS

Organization of Records. Records 1 through 10 and 13 are entered once for Data Group A. Records 11 and 12 are entered once only if the value of VFLAG entered in Record 7 is equal

to 1. If the value of VFLAG is 0, Records 11 and 12 are skipped. Record 8 uses as many lines as needed to input NPRINT1 pairs of PRINT1(I) and TPRNT1(I), 4 pairs occupying each line. Record 10 uses as many lines as needed to input NPRINT2 pairs of PRINT2(I) and TPRNT2(I), 4 pairs occupying each line. Record 12 (if needed) uses as many lines as needed to input NPRINT3 pairs of PRINT3(I) and TPRNT3(I), 4 pairs occupying each line. Record 13 will have NOSYS entries (including any "dummy" solids state variables).

2.2.2 Data Group B: Exchange (Dispersion) Coefficients

Exchange coefficients are computed from input dispersion coefficients, cross-sectional areas, and characteristic lengths. Dispersion coefficients may vary in time according to piecewise linear time functions, with groups of segment pairs having the same dispersion time function. Exchange data are read for each exchange field. Field one contains dispersion coefficients for water column exchanges. Field two contains exchange data for pore water exchange. Fields three, four and five contain sediment exchange data, with a separate field available for each solid type.

Record 1--Number of Exchange Fields (I5, 75X)

NRFLD = number of exchange fields; 1 = total constituent (dissolved, bound, and particulate) exchanges (usually water column), 2 = dissolved constituent exchanges (usually water column and/or pore water); NRFLD will generally equal 1 or 2. (I5)

It is also possible to specify exchanges to represent sediment mixing for each solids type simulated (Field 3 for Solids 1, Field 4 for Solids 2, and Field 5 for Solids 3). However, this is not generally recommended.

Chemical mixing in sediment layers (exclusive of ghost stack elements) can be specified in exchange file 1.

TITLE = name of data group (for user convenience). (75X)

If no exchange rates are to be read, set NRFLD to zero and continue with Data Group C. If NRFLD is greater than zero, Records 2 through 6 are read in and repeated as a group NRFLD times.

Record 2--Exchange Time Functions for Each Exchange Field (I5, 2F10.0)

NTEX(NF) = number of exchange time functions for field NF. If no exchange time functions are input for field NF, set NTEX to zero and continue with the next exchange field. (I5)

SCALR = scale factor for exchange coefficients. All exchange coefficients for field NF will be multiplied by this factor. (F10.0)

CONVR = conversion factor for exchanges in field NF. (F10.0)

where NF = 1, NRFLD

Record 3--Exchange Data (I5)

NORS(NT) = number of exchanges for field NF, time function NT. (I5)

where NT = 1, NTEX(NF)

Record 4--Areas, Characteristic Lengths (2F10.0, 2I5)

A(K) = area in m^2 for exchange pair K defined by JR and IR. (F10.0)

EL(K) = characteristic length in m for exchange pair K. (F10.0)

JR(K),IR(K) = segment pair between which exchange occurs. The order of the segments is unimportant. (2I5)

where K = 1, NORS(NF,NT)

Record 5--Number of Time-Breaks in the Exchange Time Function (I5)

NBRKR(NF,NT) = number of time-break points in the exchange time function. (I5)

Record 6--Piece Linear Dispersion Time Function (4(F10.0, F10.0))

RT(K) = value of dispersion coefficient in m^2/sec at time TR(K). (F10.0)

TR(K) = time in days at which the dispersion coefficient is RT(K). (F10.0)

where K = 1, NBRKR(NF,NT)

Record 7--Exchange Bypass Options (16I5)

RBY(ISYS) = exchange bypass option; 0 = exchange occurs for system ISYS; 1 = bypass exchange for system K. (I5)

where ISYS = 1, NOSYS

Organization of Records. Record 1 is entered once for Data Group B. Records 2 through 6 are repeated for each exchange field, and Records 3, 4, 5, and 6 are repeated for each time function in a given exchange field. Record 4 uses as many lines as necessary to input NORS sets of A(K), EL(K), IR(K), and JR(K) (1 set per line). Record 6 uses as many lines as needed to input NBRKR pairs of RT(K) and TR(K), (4 pairs occupying each line. After data for all exchange fields are entered, Record 7 is input on the following line with NOSYS entries.

2.2.3 Data Group C: Volumes

Segment volumes, types, and hydraulic characteristics are input by the user. The segments above and below each model segment are specified to compute sediment transport between the water and sediments and burial through each sediment layer. The user also specifies options for sediment segment volumes in response to sediment transport.

Record 1--Preliminary Data (2I5, F10.0, 60X)

IVOPT = water column volume option; 1 = constant water column volumes (water column inflows and outflows specified in Data Group D must balance); 2, 3 = water column volumes adjusted (change with time) to maintain flow continuity (water column flows specified in Data Group D need not balance). (I5)

IBEDV = sediment bed volume option; 0 = constant sediment bed volumes; 1 = sediment bed volumes change in response to sediment transport. (I5)

Surficial sediment segment volumes in IPX vary in response to sediment transport so **IBEDV must be 1**. The porosity of **all** sediment segments is always constant.

TDINTS = sediment bed control options; time-step in days for porosity computations when IBEDV = 0; time-step in days for burial and

unburial to and from deeper sediment layers when IBEDV = 1. (F10.0)

TITLE = name of data group. (60X)

Record 2--Scale Factors (2F10.0)

SCALV = scale factor for segment volumes. All volumes are multiplied by this factor. (F10.0)

CONVV = conversion factor for volumes. (F10.0)

Record 3--Segment Types and Volumes (I10, 2I5, I10, 5F10.0)

ISEG = segment number. (I10)

ITOPSG(ISEG) = segment immediately above ISEG; 0 = that there is no segment above (i.e. at a model boundary). (I5)

IBOTSG(ISEG) = segment immediately below ISEG; 0 = that there is no segment below (i.e. at a model boundary). (I5)

ITYPE(ISEG) = segment types;
1 = surface water segment,
2 = subsurface water segment,
3 = upper bed segment (Eulerian bed option),
4 = lower bed segment (Eulerian bed option)),
5 = upper bed segment (Semi-Lagrangian bed option),
6 = lower bed segment (Semi-Lagrangian bed option). (I10)

BVOL(ISEG) = volume of segment ISEG in cubic meters. (F10.0)

VMULT(ISEG) = hydraulic coefficient "a" for velocity in ISEG as a function of flow:
$v = aQ^b$
If b = 0, VMULT is a constant velocity in m/sec. (F10.0)

VEXP(ISEG) = hydraulic exponent "b" for velocity in ISEG as a function of flow (0-1). A value of 0.4 represents rectangular channels. (F10.0)

DMULT(ISEG) = hydraulic coefficient "c" for depth of ISEG as a function of flow:

$d = cQ^d$

If d = 0, DMULT is a constant depth in m. (F10.0)

DXP(ISEG) = hydraulic exponent "d" for depth of ISEG as a function of flow (0-1). A value of 0.6 represents rectangular channels. (F10.0). A value of d = 0 should be used for sediment segments.

where ISEG = 1, NOSEG

Organization of Records. Records 1 and 2 are entered once for Data Group C. Record 3 is repeated NOSEG times. If ICFL = 2 in Data Group A, volumes are read from the restart file (*.RST, where * is the input data file name), and Records 2 and 3 should not be included in the input data set.

2.2.4 Data Group D: Water Column Flows; Pore Water Flows; Settling Velocities; Resuspension Velocities; and Precipitation/Evaporation

Data Group D is used to specify the flows, sediment transport velocities, and precipitation/evaporation inputs used in the model and may be specified for any or all of several fields. Field one is for advective flows in the water column. Field two is for pore water flows. Fields three, four, and five are for settling velocities for solids types one, two, and three, respectively. Field six is for resuspension velocities and is applied to all solids types simulated. Field seven is for precipitation and evaporation. All time functions specified are treated as piecewise linear time functions.

Overall Organization of Records for Data Group D. Record 1 is read first. Data Sub-Group D1 is read next. Data Sub-Groups D2, D3, D4, D5, D6, and D7 follow in order for NFIELD = 2, 3, 4, 5, 6, and 7, respectively. Following all specified Data Groups, Record 7 is read.

Record 1--Data Input Options: Number of Flow Fields (2I5)

IQOPT = Surface Water flow (Field 1) input option:

1 = surface water flows are specified directly by user (qsurf1: mass transported by the net outflow).

2 = water column flows are specified directly by user (qsurf2: mass transported by the difference between the gross inflow minus the gross outflow).

3 = water column flows are read from a formatted file created by DYNHYD. (I5) **(Option Disabled)**

The user is required to directly input the surface water flows in IPX so **IQOPT must be 1 or 2.** All linkages to the DYNHYD hydrodynamic model have been disabled.

NFIELD = number of flow fields. Field 1 is for surface water (advective) flows. Field 2 is for pore water flows. Field 3 is for Solids 1 settling velocities. Field 4 is for Solids 2 settling velocities. Field 5 is for Solids 3 settling velocities. Field 6 is for resuspension velocities and is applied to all solids types. Field 7 is for precipitation and evaporation. If no transport fields are to be input, set NFIELD to zero and continue with Data Group E. (I5)

TITLE = name of data group. (70X)

DATA SUB-GROUP D1: FIELD ONE (WATER COLUMN) FLOWS (IQOPT = 1, 2)

Surface water flows are input as a separate time function for each inflow to the model. Each inflow is routed from a boundary (segment 0) through each water column segment water from a given source flows until it leaves the system through a boundary. All phases (dissolved, DOC-bound, and particulate) of each system simulated are transported by this field.

Record 2--Water Column Flow Time Function Specification (I5, 2F10.0)

NINQ(1) = number of time functions for Field One. If water column flows are not used, set NINQ to zero and skip to Data Sub-Group D2. (I5)

SCALQ = scaling factor. All flows in Field one are multiplied by SCALQ. (F10.0)

CONVQ = units conversion factor. (F10.0)

Record 3--Number of Flows (I5)

NOQS(1,NI) = number of segment pair interfaces (including those at boundaries) across which surface water from source NI flows . (I5)

where NI = 1, NINQ(1)

Record 4--Flow Routing (4(F10.0, 2I15))

BQ(1,NI,K) = decimal fraction of flow time function NI that flows between segment pair K defined by JQ and IQ. (F10.0)

JQ(1,NI,K) = segment water is flowing from. (I5)

IQ(1,NI,K) = segment water is flowing to. (I5)

where K = 1, NOQS(1,NI)

Record 5--Number of Breaks in Advective Time Functions (I5)

NBRKQ(1,NI) = the number of flow and time pairs used to describe piecewise linear time function NI. (I5)

Record 6--Piecewise Linear Advective Time Function (4(2F10.0))

QT(1,NI,K) = water column (advective) flow in m3/s. (F10.0)

TQ(1,NI,K) = time in days. (F10.0)

where K = 1, NBRKQ(1,NI)

Organization of Records for Data Sub-Group D1. Record 2 is input once. Records 3, 4, 5, and 6 are input once for each flow time function. Record 4 uses as many lines as needed to input NOQS sets of BQ, JQ, and IQ, with four sets per line. Record 6 uses as many lines as necessary to input NBRKQ sets of QT and TQ, with four sets on each line.

DATA SUB-GROUP D2: FIELD TWO (PORE WATER) FLOWS

Pore water flows are input as separate time functions for each inflow to the model. Each inflow is routed from a boundary (segment 0) and through the sediments. If pore water are routed to the water column, a surface water flow function must also be specified for field 1. Only the dissolved and DOC-bound phases of each systems simulated are transported by this field.

Record 2--Number of Pore Water Time Functions (I5, 2F10.0)

NINQ(2) = number of pore water time functions. If pore water flows are not used, set NINQ(2) to zero and skip to Data Sub-Group D3. (I5)

SCALQ = scaling factor for pore water flows. (F10.0)

CONVQ = units conversion factor. (F10.0)

Record 3--Number of Flows (I5)

NOQS(2,NI) = number of segment pair interfaces (including those at boundaries) across which pore water from source NI flows.

where NI = 1, NINQ(2)

Record 4--Flow Routing for Pore Water Flows (4(F10.0, 2I5))

BQ(2,NI,K) = decimal fraction of pore water flow for time function NI that flows between segment pair K defined by JQ and IQ. (F10.0)

JQ(2,NI,K) = segment pore water is flowing from. (I5)

IQ(2,NI,K) = segment pore water is flowing to. (I5)

Record 5--Number of Breaks in Pore Water Time Function (I5)

NBRKQ(2,NI) = number of pore water flow and time pairs used to describe piecewise linear time function NI. (I5)

Record 6--Piecewise Linear Pore Water Time Function (4(2F10.0))

QT(2,NI,K) = pore water flow in m3/s. (F10.0)

TQ(2,NI,K) = time in days. (F10.0)

where K = 1, NBRKQ(2,NI)

Organization of Records for Data Sub-Group D2. Record 2 is input once. Records 3, 4, 5 and 6 are input once for each pore water time function. Record 4 uses as many lines as necessary to input NOQS sets of BQ, JQ, and IQ, with four sets on each line. Record 6 uses as many lines as necessary to input NBRKQ sets of QT and TQ, with four sets on each line.

DATA SUB-GROUPS D3-D5: SEDIMENT TRANSPORT - SETTLING VELOCITIES

Settling velocities are input separately for each solids type simulated. A separate field is specified for each solid type: Data Sub-Group D3 is used to input settling velocities for solids type one; D4 for solids type two; and D5 for solids type three. Velocities may vary with time. Only the specified solids type and the chemical sorbed to that solids type are transported by each field.

Record 2--Number of Settling Velocity Time Functions (I5, 2F10.0)

NINQ(NF) = number of settling velocity time functions for Field NF. If settling velocities for a given solids type are not used, or if a solids type is not simulated, set NINQ(NF) to zero and skip to the next Data Sub-Group. (I5)

SCALQ = scaling factor for settling velocities. (F10.0)

CONVQ = units conversion factor. (F10.0)

where NF = 3, 5

Record 3--Number of Segment Pairs (I5)

NOQS(NF,NI) = number of segment surface water-surficial sediment pair interfaces across which sediments settle at the velocities specified by time function NI. (I5)

where NI = 1, NINQ(NF)

Record 4--Areas for Settling (4(F10.0, 2I5))

BQ(NF,NI,K) = area in m^2 between segment pair K defined by JQ and IQ. (F10.0)

JQ(NF,NI,K) = water column segment that solids type (NF-2) settles from. (I5)

IQ(NF,NI,K) = surficial sediment segment that solids type (NF-2) settles to. (I5)

where K = 1, NOQS(NF,NI)

Record 5--Number of Breaks in Velocity Time Function (I5)

NBRKQ(NF,NI) = number of settling velocity and time pairs used to describe piecewise linear time function NI. (I5)

Record 6--Piecewise Linear Settling Velocity Time Function (4(2F10.0))

QT(NF,NI,K) = settling velocity in m/s. (F10.0)

TQ(NF,NI,K) = time in days. (F10.0)

where K = 1, NBRKQ(NF,NI)

Organization of Records for Data Sub-Groups D3-5. Records 2 through 6 are input for each solid type. Records 3, 4, 5 and 6 are input for each time function in each field. Record 4 uses as many lines as needed to input NOQS sets of BQ, JQ, and IQ, with four sets on one line. Record 6 uses as many lines as needed to input NBRKQ sets of QT and TQ, with four sets per line.

DATA SUB-GROUPS D6: SEDIMENT TRANSPORT - RESUSPENSION VELOCITIES

Resuspension velocities are input once and applied to each solids type simulated. One field is specified for all solid types; Data Sub-Group D6 is used to input all resuspension velocities. Velocities may vary with time. All solids simulated and the chemical sorbed to each solid type are transported by this field.

Record 2--Number of Resuspension Velocity Time Functions (I5, 2F10.0)

NINQ(6) = number of resuspension velocity time functions for Field NF. If resuspension velocities are not used, or if solids are not simulated, set NINQ(6) to zero and skip to Data Sub-Group D7. (I5)

SCALQ = scaling factor for resuspension velocities. (F10.0)

CONVQ = units conversion factor. (F10.0)

Record 3--Number of Segment Pairs (I5)

NOQS(6,NI) = number of surficial sediment-surface water segment pair interfaces across which sediments resuspend at the velocities specified by time function NI. (I5)

where NI = 1, NINQ(6)

Record 4--Areas for Resuspension (4(F10.0, 2I5))

BQ(6,NI,K) = area in m^2 between segment pair K defined by JQ and IQ. (F10.0)

JQ(6,NI,K) = surficial sediment segment that solids resuspend from. (I5)

IQ(6,NI,K) = water column segment that solids resuspend to. (I5)

where K = 1, NOQS(6,NI)

Record 5--Number of Breaks in Velocity Time Function (I5)

NBRKQ(6,NI) = number of resuspension velocity and time pairs used to describe piecewise linear time function NI. (I5)

Record 6--Piecewise Linear Resuspension Velocity Time Function (4(2F10.0))

QT(6,NI,K) = resuspension velocity in m/s. (F10.0)

TQ(6,NI,K) = time in days. (F10.0)

where K = 1, NBRKQ(6,NI)

Organization of Records for Data Sub-Group D6. Records 2 is input once. Records 3, 4, 5 and 6 are input for each time function in each field. Record 4 uses as many lines as needed to input NOQS sets of BQ, JQ, and IQ, with four sets on one line. Record 6 uses as many lines as needed to input NBRKQ sets of QT and TQ, with four sets per line.

DATA SUB-GROUP D.7: PRECIPITATION AND EVAPORATION

Precipitation and evaporation data are input to represent rainfall, seasonal evaporation, or other events that change surface water levels. In response to the specified time functions water volumes are adjusted to maintain continuity. In addition to modifying water volumes, chemicals and solids are transported into the model by precipitation. **However, since only one boundary condition can be specified per model segment, it is recommended that all contaminant inputs resulting from precipitation be treated as loads.** No chemical or solids mass is transported out of the model by evaporation.

Record 2--Number of Precipitation/Evaporation Time Functions (I5, 2F10.0))

NINQ(7) = number of precipitation and evaporation time functions. (I5)

SCALQ = scaling factor for precipitation/evaporation. (F10.0)

CONVQ = units conversion factor. (F10.0)

Record 3--Number of Segment Pairs (I5)

NOQS(7,NI) = number of surface water segment-air interfaces across which water precipitates/evaporates at the rate specified by time function NI. (I5)

Record 4--Areas for Precipitation/Evaporation (4(F10.0, 2I5))

BQ(7,NI,K) = area in m^2 between segment pair K defined by JQ and IQ. (F10.0)

JQ(7,NI,K) = segment water is transported from; use JQ = 0 to represent precipitation. (I5)

IQ(7,NI,K) = segment water is transported to; use IQ = 0 to represent evaporation. (I5)

where K = 1, NOQS(7,NI)

Record 5--Number of Breaks in Precipitation/Evaporation Time Function (I5)

NBRKQ(7,NI) = number of precipitation/evaporation rate and time pairs used to describe piecewise linear time function NI. (I5)

Record 6--Piecewise Linear Precipitation/Evaporation Time Functions (4(2F10.0))

QT(7,NI,K) = precipitation/evaporation rate in m/s; if more traditional units of cm/day or cm/year are desired, then specify CONVQ = 1.1574E-7 or 3.169E-10, respectively. (F10.0)

TQ(7,NI,K) = time in days. (F10.0)

where K = 1, NBRKQ(7,NI)

--End of Data Sub-Groups For Data Group D--

Record 7--Transport (Data Group D) Bypass Options (16I5)

QBY(ISYS) = transport bypass option for system ISYS; 0 = system will be transported; 1 = system will be not be transported. The bypass option applies to transport by all fields. (I5)

where ISYS = 1, NOSYS

2.2.5. Data Group E: Boundary Concentrations

Data Group E is repeated, in its entirety, NOSYS times. No boundary conditions are specified for the bottom segment in any stack of sediments using the semi-Lagrangian sediment bed option.

Record 1--Number of Boundary Conditions (I10, 70X)

NOBC(ISYS) = number of boundary conditions used for system ISYS. If no boundary conditions are to be input for System ISYS, set NOBC(ISYS) equal to zero and continue entering boundary conditions for the next system. When boundary conditions for all systems have been specified (or skipped by setting NOBC(ISYS) to zero) skip to Data Group F. (I10)

TITLE = name of data group. (70X)

where ISYS = 1, NOSYS

Record 2--Scale Factor for Boundary Conditions (2F10.0)

SCALB = scale factor for boundary conditions for System ISYS. All boundary conditions for System ISYS will be multiplied by this factor. (F10.0)

CONVB = unit conversion factor for boundary conditions for System ISYS. Boundary conditions are expected to be in milligrams per liter (mg/L). (F10.0)

Record 3--Boundary Conditions (2I5)

IBC(ISYS,NB) = boundary segment number. (I5)

NOBRK(ISYS,NB)= number of boundary condition value and time pairs used to describe the boundary condition. (I5)

where NB = 1, NOBC

Record 4--Boundary Concentrations Time Function(4(2F10.0))

BCT(ISYS,NB,K) = boundary concentration in mg/L at time T(K) for segment IBC. (F10.0)

T(ISYS,NB,K) = time in days. If the length of the simulation exceeds T(ISYS,NB,NOBRK), the function is assumed to be periodic and repeated, starting at T(1) with period equation to T(ISYS,NB,NOBRK). (F10.0)

where K = 1, NOBRK

Organization of Records for Data Group E. Records 1 and 2 are entered once. Records 3 and 4 are a set and are repeated NOBC times. Within each NOBC set, Record 3 is entered once and Record 4 is repeated until NOBRK entries are input. Four entries (four BCT(K)-T(K) pairs) will fit on each 80-space line. The whole group is repeated NOSYS times, once for each model system. Boundary conditions are never specified for ITYPE = 5 or ITYPE = 6 sediment segments (see description of semi-Lagrangian bed option).

2.2.6 Data Group F: Point and Non-Point Source Loads (Forcing Functions)

Data Group F is used to specify point and non-point source loads (forcing functions) used in the model. Point source forcing functions are specified in Data Sub-Group F1. Non-point forcing functions are specified in Data Sub-Group F2.

Overall Organization of Records for Data Group F. Data Sub-Group F1 is read first and is repeated once for each system simulated. Data Sub-Group F2 is read second.

DATA SUB-GROUP F1: POINT SOURCE LOADS

Data Sub-Group F1 is used to input all point source waste loads in the model. Data Sub-Group F1 is repeated NOSYS times.

Record 1--Number of Forcing Functions (I10, 70X)

NOWK(ISYS) = number of forcing functions for System ISYS. Forcing functions specified as sources (+) or sinks (-) of a water quality constituent

(system). If forcing functions are not input, set NOWK(ISYS) to zero, and continue with next system or go to next data group.(I10)

TITLE = name of data group. (70X)

Record 2--Forcing Function Scale and Conversion Factors (2F10.0)

SCALW = scale factor for forcing functions. All forcing functions will be multiplied by this factor. (F10.0)

CONVW = unit conversion factor for forcing functions. Forcing functions are expected to be in kilograms per day. If forcing functions are given in English units (pounds per day), this factor will be 0.4535. (F10.0)

Record 3--Number of Point Sources (2I5)

IWK(NW) = segment number to which forcing function WKT(K) is applied. (I5)

NOBRK(NW) = number of forcing function and time value pairs used to describe the forcing function WKT(K). (I5)

where NW = 1, NOWK

Record 4--Point Source Time Function (4(2F10.0))

WKT(K) = value of the forcing function at time T(NW,K), in kg/day. (F10.0)

T(K) = time in days. If the length of the simulation exceeds T(NOBRK), the approximation is assumed to be periodic and is repeated starting at T(1) with a period equal to T(NOBRK). (F10.0)

where K = 1, NOBRK

Organization of Records for Data Sub-Group F1. Records 1 and 2 are input once. Records 3 and 4 are a set and repeated as a set NOWK times. Within each set, Record 3 is input once and Record 4 is repeated until all NOBRK entries are input (four WKT(K), T(K) pair entries per line). Data Sub-Group F1 is repeated NOSYS times, once for each system.

DATA SUB-GROUP F2: NON-POINT SOURCE LOADS (FORCING FUNCTIONS)

Data Sub-Group F2 allows the user non-point source loads that are read in from an external file named NPS.DAT that must be created prior to running the model.

The authors recommend that all non-point source loads be treated as point source loads and input through Data Sub-Group F1. This non-point load option was originally developed to allow WASP4 users to link water quality simulation to storm water/runoff models such as SWMM. However, code operation for computing non-point source forcing functions has not been verified.

Record 1--Number of Runoff Loads, Initial Day (2I5)

NOWKS = number of segments receiving runoff loads. If non-point source loads are not specified, set NOWKS equal to zero and skip to Data Group G. If NOWKS > 0, continue with records 2, 3, and 4. (I5)

NPSDAY = the time in the runoff file corresponding to the initial simulation time, in days. (I5)

Record 2--Scale Factor for Runoff Loads (2F10.0)

SCALN = scale factor for runoff loads. All runoff loads will be multiplied by this factor. (F10.0)

CONVN = unit conversion factor for runoff loads. Runoff loads are expected in kilograms per day. If runoff loads are given in English units (pounds per day), this factor will be 0.4535. (F10.0)

Record 3--Runoff Segments (16I5)

INPS(J) = segment number to which runoff load J is applied. (I5)

where J = 1,NOWKS

Record 4--Print Specifications (16I5)

KT1 = initial day for which nonzero runoff loads from file NPS.DAT will be printed. (I5)

KT2 = final day for which nonzero runoff loads from file NPS.DAT will be printed. (I5)

KPRT(I) = indicator specifying whether nonzero runoff loads will be printed for each system. If KPRT(I) is greater than zero, then runoff loads will be printed for system I. (I5)

where I = 1,NOSYS

Organization of Records for Data Sub-Group F2. Records 1 and 2 are input once. Record 3 has NOWKS entries and uses as many 80-space lines as needed to enter all NOWKS segment numbers (16 entries will fit on one line). Record 4 is input once.

2.2.7 Data Group G: Parameters

Data Group G is used to enter all environmental parameters required for a simulation. The number of parameters needed for any simulation will vary as a function of the type of water body modeled and the simulation complexity. The input format for all parameters, however, is constant.

Record 1--Number of Parameters (I10, 70X)

NOPAM = number of parameters used in the simulation. If no parameters are specified, set NOPAM to zero and skip to Data Group H. (I10)

TITLE = name of data group. (70X)

Record 2--Scale Factors for Parameters (4(A5, I5, F10.0)

ANAME(ISC) = descriptive name for parameter ISC. (A5)

ISC = parameter number identifying parameter; all parameter numbers are defined in Table 2.2. (I5)

PSCAL(ISC) = scale factor for parameter ISC that will be applied to parameter ISC in all segments. (F10.0)

where ISC = 1, NOPAM

Record 3--Segment Number (I10)

ISG = model segment number to which the following parameter values will be applied. (I10)

Record 4--Segment Parameters (4(A5, I5, F10.0))

PNAME(ISC) = an optional one to five alphanumeric character descriptive name used to identify PARAM(ISG,ISC). (A5)

ISC = parameter number identifying the parameter; all parameter numbers are defined in Table 2.2. (I5)

PARAM(ISEG,K) = the value of parameter ISC in segment ISG. (F10.0)

where K = 1, NOPAM

ISEG = 1, NOSEG

Organization of Records for Data Group G. Record 1 is input once and occupies one line. Record 2 has NOPAM entries. Four entries will fit on one line; thus, Record 2 uses as many 80-space lines as needed to enter all NOPAM entries. Records 3 and 4 are entered NOSEG times, once for each segment. For each segment, Record 4 uses as many lines as needed to enter all NOPAM entries.

2.2.8 Data Group H: Physicochemical Constants

Data Group H is used to enter all chemical specific physicochemical constants required for a simulation. The number of constants needed for any simulation will vary as a function of the type of water body modeled and the kinetic complexity of the simulation.

The structure of Data Group H varies. This data group is subdivided into constants that are applied to individual chemicals or solids (systems) and global constants that are applied to all systems (thus NOSYS+1 sub-groups of constants are read). Each sub-group can be further subdivided into a user specified arbitrary number of sets that contain similar kinds of data that allows the user to logically organize all Data Group H inputs.

Record 1--Header (80X)

TITLE = name of data group. (80X)

Record 2--Data Fields in Group K (A10, I10)

CHNAME(ISYS) = ten-character descriptive name for System ISYS. (A10)

NFLD = number of groups of constants for System ISYS; 0 = no constants for this System (skip to next System); the user may subdivide the constants into any number of arbitrary groups. (I10)

where ISYS = 1, NOSYS+1

Groups for ISYS=1-NOSYS are for input of constants that apply to an individual system (chemical or solids. The group for ISYS=NOSYS+1 is for input of global constants.

Record 3--Number of Constants in Group (A10, I10)

FLDNAME = ten-character name identifying field of constants. (A10)

NCONS = number of constants to be entered in this group; 0 = no constants for this group (skip to next field). (I10)

Record 4--Constants (2(A10, I10, F10.0))

TNAME(ISC) = name identifying constant ISC. (A10)

ISC = number identifying constant; all constant numbers are defined in Tables 2.3-2.12. (I10)

CONST(ISC) = value of constant ISC in units specified in Tables 2.3-2.12. (F10.0)

Record 5--Reaction Yields (I10)

NYLDS = total number of reaction yields (I10)

Reaction yields must be specified anytime a simulated chemical undergoes a reaction through which it is transformed into a chemical that is also simulated. If a chemical reacts and is transformed into a state that is not being simulated, no reaction yield will be specified.

Record 6--Yield Constants (2(3I5, F10.0))

FROM = reacting chemical number; Chemicals 1 to N are Systems 4 to (N+3). (I5)

TO = product chemical number. (I5)

The chemical number into which reacting chemicals are transformed is never zero (to represent transformation to a chemical state not simulated). If chemical reactions transform a model state variable into a product that is not also being simulated, no reaction yield is specified.

PROCESS = reaction process pathway number. (I5)

1 = water column biodegradation
2 = benthic biodegradation
3 = alkaline hydrolysis
4 = neutral hydrolysis
6 = oxidation
7 = photolysis
8 = extra (user defined) reaction

Y = reaction yield constant in gram product chemical produced/gram reacting chemical reacted. (F10.0)

Organization of Records for Data Group H. Record 1 is input once. Records 2 through 4 are input for NOSYS +1 groups, one for each modeled system (1 to NOSYS) and one for global constants (NOSYS+1). For each group, Records 3 and 4 are entered NFLD times. For each field, Record 4 uses as many lines as needed for NCONS entries (2 entries per line). Record 5 is input once. Record 6 uses as many lines as needed for NYLDS entries (2 entries per line).

2.2.9 Data Group I: Kinetic Time Functions

Data Group I is used to enter all kinetic time functions required for a simulation. The number of kinetic time functions needed for any simulation will vary as a function of the simulation complexity. The input format for all time functions, however, is constant.

Record 1--Number of Time Functions (I10, 70X)

NFUNC = number of time functions used in the simulation. If no time functions are specified, set NFUNC to zero and skip to Data Group J. (I10)

TITLE = name of data group. (70X)

Record 2--Time Function Descriptions (A5, 2I5)

ANAME(ISC) = an optional one to five alphanumeric character descriptive name for the time function ISC(I). (A5)

ISC(I) = number identifying the time function; all time function numbers are defined in Table 2.13. (I5)

NOBRK(ISC) = number of breaks used to describe the time function ISC(I). (I5)

where I = 1, NFUNC

Record 3--Time Functions (4(2F10.0))

VALT(K) = value of time function ISC(I) at time T(K). (F10.0)

T(K) = time in days. If the length of the simulation exceeds T(NOBRK), the time function is assumed to be periodic and is repeated starting at T(1) with a period equal to T(NOBRK). (F10.0)

where K = 1, NOBRK

Organization of Records for Data Group I. Record 1 is input once. Records 2 and 3 are a set and repeated as a set NFUNC times. Within each set, Record 2 is input once and Record 3 is repeated until all NOBRK entries are input (four VALK(K)-T(K) pair entries per line).

2.2.10 Data Group J: Initial Concentrations

Data Group J is used to specify the concentrations of each system in each model segment at the start of the simulation. Conditions specified are the segment concentrations and densities for the state variables at the simulation start time (ZDAY+ZHOUR/24+ZMIN/1440) specified in Data Group A. If ICFL = 2 in Data Group A, initial concentrations are read from the restart file.

Even if initial conditions are to be read from a restart file, it is still necessary to include Data Group J in the input data set to allow proper read in of Data Group K.

Record 1--System Information (A40, I5, F5.0, F10.0, 20X)

CHEML = system name (chemical or solid). (A40)

IFIELD = solids field (3, 4, or 5) that transports this system in its pure or sorbed form (I5).

Previous versions of the WASP4 framework from which IPX was derived were developed to simulate eutrophication. For the eutrophication version of the framework, IFIELD was used to specify which the settling velocity field in Data Group D was used to transport planktonic solids. For IPX simulations, set IFIELD to 3 for solids type 1, 4 for solid 2, and 5 for solid 3; set IFIELD to 1 for all chemical systems simulated.

DSED = density of system in kg/L; choose 0.5-2.5 for solids; choose 0.0 for chemicals. (F5.0).

CMAX = maximum concentration of system permitted during the simulation in mg/L; if the computed concentration ever exceeds CMAX, the simulated is aborted. (F10.0)

TITLE = name of data group. (20X)

Record 2--Initial Conditions (3(A5, 2F10.0)

ANAME(ISEG) = an optional one to five alphanumeric character descriptive name or number identifying segment ISEG. (A5)

C(ISYS,ISEG) = initial concentration of system ISYS in segment ISEG in mg/L. (F10.0)

DISSF = dissolved fraction of chemical in segment K. (F10.0)

The value specified for DISSF is unimportant. The fractions of chemical in each phase (dissolved, DOC bound, or particulate) are

computed as a function of partition coefficients specified in Data Group H. (If no partitioning constants are specified, all chemical mass will be in the dissolved phase.)

where ISEG = 1, NOSEG

ISYS = 1, NOSYS

Organization of Records for Data Group J. Records 1 and 2 are a set and repeated as a set NOSYS times. Within each set Record 2 is repeated until NOSEG entries are input (three ANAME-C-DISSF entries per line).

2.2.11 Data Group K: Surficial Sediment Age Layer Conditions

Data Group K is used to specify the surficial sediment aging control parameters used throughout the simulation and the initial distribution of sediments in each surficial sediment age layer at the start of the simulation.

Record 1 -- Sediment Aging Information (A40,2I5,F10.0,10X)

SOLNAME = Data Group name for user reference. (A40)

NSURFSEDS = number of surficial sediment segments in the model (segments with ITYPE = 3 or 5). (I5)

NSEDAGES = Number of age layers in the sediments. (I5)

TSEDAGES = time for sediment aging computations, in days. (F10.0)

Record 2 -- Sediment Age Layer Initial Conditions (A5,(NSEDAGES(F10.0))

BNAME(I) = identifier of surficial sediment segment I for user reference. (A5)

LAYERDEP(I,J) = depth of sediment in age layer J of segment I, in cm. (F10.0). The sum of the nSedAges layerDep values should equal the segment depth (d) defined for each surficial sediment segment in Data Group C (volumes):

$$d_I = \sum_{J=1}^{nSedAges} layerDep(I,J)$$

where I = 1, NSURFSEDS

where J = 1, NSEDAGES

Record 3 -- Sediment Resuspendability Control Parameters (A5,F10.0)

CNAME(J) = Name of age layer J for user reference. (A5)

TDEPOSITION(J) = sediment resuspendability factor for age layer J (the value of parameter Z in the epsilon equation, Equation 1.25). (F10.0)

where J = 1, NSEDAGES

Record 4 -- Fresh Sediment Resuspension Control Parameters (3F10.0)

A0 = fresh sediment resuspension coefficient (fresh sediments only). (F10.0)

M = fresh sediment resuspension exponent (fresh sediments only). (F10.0)

TAUCRIT = critical shear for fresh sediment resuspension, in dynes/cm^2 (fresh sediments only). (F10.0)

Organization of Records for Data Group K. Record 1 is input once. Record 2 is repeated for each surficial sediment segment (ITYPE = 3 or 5) in the model with nSedAges initial age layer depths appearing on each line. Record 3 is repeated for each sediment age layer. Record 4 is input once.

Example: Data Group K. Data Group K, from an IPX input data file used to model sediment transport in the Fox River, is listed below to illustrate the specification of sediment resuspension parameters:

```
 Surficial Sediment Age Layer Conditions   48    7       1.0
Seg25         1         1         1         1         1         1         4
⋮
(lines for Segments 26 thru 71 deleted)
⋮
Seg72         1         1         1         1         1         1         4
```

```
Layr1      1.00
Layr2      1.00
Layr3      1.00
Layr4      1.00
Layr5      1.00
Layr6      1.00
Layr7      1.00
     0.008        3.         1.
```

2.2.12 Data Group L: Initial Conditions for Deep Sediment Layers (Ghost Stack) (Semi-Lagrangian Bed Option)

Data Group L is used to specify control parameters and initial conditions for sediment compartments comprising the ghost stack using the semi-Lagrangian sediment bed option. If there is at least one surficial sediment segment specified as ITYPE = 5, the semi-Lagrangian sediment bed option is enabled and Data Group L must be entered. Data Group L is skipped only if there are no segments specified as ITYPE = 5. Note that if no segments are specified as ITYPE = 5, then there should not be any segment specified as ITYPE = 6.

Record 1 -- Minimum and Maximum Thickness (Volume) Control Parameters (2F10.0)

MINDEP = Minimum depth factor to trigger upward sediment re-indexing

MAXDEP = Maximum depth factor to trigger downward sediment re-indexing

Record 2 -- Ghost Stack Configuration Information (3I5)

SEGNUM = Surface sediment segment number (dummy variable just for user reference). (I5)

NGHOST0(ISEG) = Number of elements in ghost stack under surface sediment segment ISEG at the start of the simulation (do not include subsurface segments specified in Data Group C). (I5)

IGOPT(ISEG) = Ghost collapse option flag. (I5)

0 = Ghost collapse option off. Ghosts do not collapse.
1 = Ghost collapse option on. Ghost collapse enabled.

Record 3 -- Ghost Stack Element Geometry (2F10.0)

AG0(ISEG,IG) = Surface area of ghost stack element IG under segment ISEG in m^2. (F10.0)

DG0(ISEG,IG) = Thickness of ghost stack element IG under segment ISEG in meters. (F10.0)

Record 4 -- Ghost Stack Element State Variable Concentrations (8F10.0)

CG(ISYS,ISEG,IG)= Concentration of state variable ISYS in ghost stack element IG under surface segment ISEG in mg/L. (F10.0)

where ISYS = 1, NOSYS

IG = 1, NGHOST0

ISEG = 1, NOSEG for all ISEG where ITYPE = 5

Organization of Records for Data Group L. Record 1 is input once. Record 2 is input once for each semi-Lagrangian sediment stack (surficial sediment segment specified as ITYPE = 5) in the model with nSedAges initial age layer depths appearing on each line. Records 3 and 4 are repeated once for each ghost element in the stack. Record 4 takes as many lines as are needed to input values for all state variables with a maximum of 8 values per line. If the initial number of occupied ghost elements in any stack is zero, only Record 2 is input for that stack.

2.3 IPX MODEL PARAMETERS, CONSTANTS, AND TIME-FUNCTIONS OVERVIEW

The environmental parameters, physicochemical constants, and time functions that may be specified in Data Groups G, H, and I are described in the following sections. The number of parameters, constants, and time functions that the user must specify depends on the complexity with which chemical reactions and the interactions between chemicals and solids are to be simulated. For convenience, the complexity necessary to represent environmental dynamics has been conceptually divided into the five equilibrium and four kinetic complexity levels presented in Table 2.1. These complexity levels are best conceptualized as points along a spectrum of possible simulation complexities; not all chemicals simulated will, or need be, simulated at the same complexity. However, more complex representations of environmental dynamics generally require more constants than simpler representations.

Table 2.1. Conceptual levels of simulation complexity.

Complexity Level	Explanation
Equilibrium 1	Constant partition coefficient (K_p = constant)
Equilibrium 2	Variable partition coefficients (K_p = f(x, y, z, t)
Equilibrium 3	Hydrophobic partitioning ($K_p = K_{oc}\ f_{oc}$)
Equilibrium 4	Hydrophobic, solids-dependent partitioning (K_p = f(K_{oc}, f_{oc}, m_1))
Kinetic 1	Constant process half-life or rate constants
Kinetic 2	Variable process rate constants
Kinetic 3	Second-order process rates (rates depend on specified physical characteristics of the modeled system)
Kinetic 4	Chemical reactions that yield transformation products that are simulated chemical state variables

2.3.1 Environmental Parameters: Data Group G

The 16+ environmental parameters the user can specify are listed in Table 2.2. These parameters permit the user to spatially vary the environmental properties that control the rates at which simulated chemicals react. The user need input only those parameters required to represent the particular reactions simulated. It is not necessary to specify any parameters unless required to represent a specific mass transport pathway. The parameters specified in Data Group G are coupled with the time functions in Data Group I to permit simultaneous spatial and temporal variation of simulation conditions.

No parameters are necessary for Equilibrium Level 1. At this complexity level, all partitioning coefficients for each chemical are constant and best specified in Data Group H. For equilibrium level 2 FOC(ISEG,1), FOC(ISEG,2), and FOC(ISEG,3) can be used as dimensionless multipliers of the partition coefficients input in Data Group H. For equilibrium levels 3 and 4, FOC(ISEG,1), FOC(ISEG,2), and FOC(ISEG,3) are the fraction organic carbon of each solids class. DOC(ISEG) may be entered to represent three-phase partitioning.

No parameters are necessary for Kinetic Level 1. At this complexity level, all reaction rates for each chemical are constant and best specified in Data Group H. At kinetics level 2, TOTKG(ISEG,1), TOTKG(ISEG,2), and TOTKG(ISEG,3) can be used as dimensionless

Table 2.2. Data Group G environmental parameters.

ISC	PARAM (ISEG,ISC)	Definition, Units, Reactions Affected
1	VELFN (ISEG)	Pointer to water velocity time function (1-4) that will be specified in Data Group I; V.
2	TMPFN (ISEG)	Pointer to water temperature time function (1-4) that will be specified in Data Group I; ALL.
3	TEMP (ISEG)	Water temperature in segment (°C) and/or multiplier for the selected water temperature time function (TEMPN); ALL.
4	WVEL (ISEG)	Wind velocity over segment (m/s) and/or multiplier for WIND time function; V.
5	REAR (ISEG)	Oxygen reaeration in segment (m/d) and/or multiplier of REARN time function; usage depends on volatilization option selected; V.
6	DOC (ISEG)	Dissolved organic carbon concentration in segment (mg/L); S, P.
7	FOC (ISEG,1)	Fraction organic carbon of solids type 1 in segment and/or multiplier of MFOC(1) time function; S.
8	FOC (ISEG,2)	Fraction organic carbon of solids type 2 in segment and/or multiplier of MFOC(2) time function; S.
9	FOC (ISEG,3)	Fraction organic carbon of solids type 3 in segment and/or multiplier of MFOC(3) time function; S.
10	CHPHL (ISEG)	Chlorophyll concentration in segment and/or multiplier for CHLN time function (mg/L); P.
11	PH (ISEG)	pH in segment and/or multiplier for pH time functions (PHNW and PHNS); H.
12	XKE2 (ISEG)	Light extinction coefficient of photochemically active light in segment (1/meter); P.
13	OXRAD (ISEG)	Concentration of oxidants in segment, such as O_3 for H_2O_2 (moles/L); O.

S = sorption; V = volatilization; B = biodegradation; H = hydrolysis; O = oxidation; P = photolysis; E = extra (user defined) reaction

Table 2.2 (continued). Data Group G environmental parameters.

ISC	PARAM (ISEG,ISC)	Definition, Units, Reactions Affected
14	BAC (ISEG)	Density of active bacteria (cells/100 cc) in segment and/or multiplier of bacteria time functions (BACNW and BACNS). Units for BAC must be consistent with those of KBIO20 (constants 146-160); the product of BAC and KBIO20 must yield units of day-1; B.
15	EXENV (ISEG)	Environmental property that affects the user-defined "extra reaction." Units for EXENV must be consistent with those of KE20 (constants 576-590); the product of EXENV and KE20 must yield units of day^{-1}; E.
16 - N	TOTKG (ISEG,N)	Total lumped first-order decay rate constant for chemical (N-15) (day^{-1}). where N = 15 + number of chemicals simulated

S = sorption; V = volatilization; B = biodegradation; H = hydrolysis; O = oxidation; P = photolysis; E = extra (user defined) reaction

multipliers of the overall reaction rates input in Data Group H. Kinetics level 3 may require the other parameters, depending on the kinetic processes of importance. For example, if water temperatures differ significantly from 20˚C, then it may be necessary to input TEMP(ISEG) to properly represent reaction processes. If volatilizing chemicals are simulated, it may be necessary, or required, to input REAR(ISEG), DEPTH(ISEG), VELOC (ISEG) or WVEL (ISEG), etc. In general, if a chemical reaction pathway is a function of a physical property of the water body, it may be necessary to specify one or more parameters.

2.3.2 Physicochemical Constants: Data Group H

The physicochemical constants the user can specify are listed in Tables 2.3-2.12. These constants permit the user to specify chemical-specific properties that control the rates at which simulated chemicals react. The user need input only those constants required to represent the particular equilibria and reactions simulated. It is not necessary to specify any parameters for any solids class simulated. For each chemical it is almost always necessary to specify the molecular weight (constant 81). Beyond the molecular weight, it is not necessary to specify any additional constants unless required to represent a specific mass transport or reaction pathway. The

Table 2.3. Partition coefficients and rate constants for simple reactions.

Constant	Variable	Definition
111	PIXC(1,1)	Constant partition coefficient (K_{p1}) for sorption to solids class 1, L_w/kg_s
116	PIXC(2,1)	Constant partition coefficient (K_{p2}) for sorption to solids class 2, L_w/kg_s
121	PIXC(3,1)	Constant partition coefficient (K_{p3}) for sorption to solids class 3, L_w/kg_s
	K_i	*General first-order loss rate constants, day^{-1}*
140	KV	Volatilization
141	KBW	Water column biodegradation
142	KBS	Benthic (sediment) biodegradation
181	KHOH	Alkaline hydrolysis
182	KHN	Neutral hydrolysis
183	KHH	Acid hydrolysis
256	KO	Oxidation
287	KF	Photolysis
571	KE	Extra (user defined) reaction
	TH_i	*General reaction half-life, day*
143	THBW	Water column biodegradation
144	THBS	Benthic biodegradation
252	THHOH	Alkaline hydrolysis
253	THHN	Neutral hydrolysis
254	THHH	Acid hydrolysis
257	THO	Oxidation
289	THF	Photolysis
572	THE	Extra (user defined) reaction

Table 2.4. General chemical constants.

Constant	Variable	Definition
3	VB	LeBas molar volume, cm^3/mol
4	TMELT	Melting temperature, ˚C
9	TDINT	Time interval at which reaction rates are recomputed, days
81	MOLWT	Molecular weight, g/mole
82	SOLG	Solubility, mg/L
83	VAPRG	Vapor pressure, atm
84	LKOW	*Log* octanol-water partition coefficient, L_{oct}/L_{water}

Table 2.5. Sorption constants.

Constant	Variable	Definition
84	LKOW	*Log* octanol-water partition coefficient, L_{water}/L_{oct}
101	LKOC	*Log* of the organic carbon partition coefficient, L_{water}/kg_{oc}; for hydrophobic solids dependent partitioning, this is *log* K_{oc} at zero solids concentration.
102	A0	Intercept in the K_{ow} - K_{oc} correlation: *log* Koc = A_0; *log* K_{ow} + A_1; default A_0 = log 0.6
103	A1	Slope in the Kow - Koc correlation; default = 1.0
106	NUX(1)	Solids-dependent partitioning parameter (ν_x) of the chemical onto solids; default = 10^{12} makes K_p independent of solids concentration
111	PIXC(1,1)	Solids-independent (limiting) partition coefficient K_{p0} for sorption to solid 1, (L_{water}/kg_{solids}); if PIXC is not specified, K_{p0} for the chemical will be calculated from LKOC and parameter FOC
116	PIXC(2,1)	Solids-independent (limiting) partition coefficient K_{p0} for sorption to solid 2, (L_{water}/kg_{solids})
121	PIXC(3,1)	Solids-independent (limiting) partition coefficient K_{p0} for sorption to solid 3, (L_{water}/kg_{solids})

Table 2.6. Hydrolysis constants.

Constant	Variable	Definition
603	XHYDRO	Hydrolysis Option: 0 = No hydrolysis 1 = Hydrolysis occurs
Neutral pH (pH ≈ 7.0)		
184	TREFH	Reference temperature at which hydrolysis rates were measured, °C
201	KH2O(2,1,1)	20°C neutral hydrolysis rate constant for dissolved chemical, day^{-1}
206	KH2O(2,2,1)	20°C neutral hydrolysis rate constant for DOC-bound chemical, day^{-1}
211	KH2O(2,3,1)	20°C neutral hydrolysis rate constant for particulate chemical, day^{-1}
236	EHN(1)	Activation energy for neutral hydrolysis, kcal/mole
Acid pH (pH < 7)		
216	KH2O(3,1,1)	Second-order, 20°C acid hydrolysis rate constant for dissolved chemical, L/mole-day
221	KH2O(3,2,1)	Second-order, 20°C acid hydrolysis rate constant for DOC-bound chemical, L/mole-day
226	KH2O(3,3,1)	Second-order, 20°C acid hydrolysis rate constant for particulate chemical, L/mole-day
241	EHH(1)	Activation energy for acid hydrolysis, kcal/mole
Alkaline pH (pH > 7)		
186	KH2O(1,1,1)	Second-order, 20°C alkaline hydrolysis rate constant for dissolved chemical, L/mole-day
191	KH2O(1,2,1)	Second-order, 20°C alkaline hydrolysis rate constant for DOC-bound chemical, L/mole-day
196	KH2O(1,3,1)	Second-order, 20°C alkaline hydrolysis rate constant for particulate chemical, L/mole-day
231	EHOH(1)	Activation energy for alkaline hydrolysis, kcal/mole

Table 2.7. Photolysis constants.

Constant	Variable	Definition
286	XPHOTO	Photolysis option: 0 = no photolysis 1 = depth-integrated photolysis rate input by user
291	KDPG(1)	Depth-integrated photolysis rate (m/day)
551	QUANTG(1)	Quantum yield fraction of dissolved chemical
556	QUANTG(2)	Quantum yield fraction of particulate chemical
561	QUANTG(3)	Quantum yield fraction of DOC-bound chemical

Table 2.8. Global constants (generally not used at this time).

Constant	Variable	Definition
1	TO	Julian date at beginning of simulation
3	ELEVG	Average ground surface elevation, m
4	LATG	Latitude of water body, degrees
6	XLITE	Water surface light intensity option; 0 = do not compute light; 1 = annual average; 2 = average for month indicated by TO; 3 = monthly step function
7	DFACG	Ratio of optical path length to vertical depth; 1.17
11-23	CLOUDG(1)	Mean monthly cloudiness, in tenths of full sky coverage (0-10)
24-36	AIRTYG(1)	Mean monthly air mass type; 1 = rural, 2 = urban, 3 = maritime, 4 = tropospheric
37-49	RHUMG(1)	Mean monthly daylight relative humidity, percent
50-62	ATURBG(1)	Mean monthly atmospheric turbidity, in equivalent aerosol layer thickness km
63-75	OZONEG(1)	Mean monthly ozone content of atmosphere, in cm NTP (0.2 - 0.3)

Table 2.9. Oxidation constants.

Constant	Variable	Definition
604	XOXID	Oxidation Option: 0 = No oxidation 1 = Oxidation occurs
258	TREFO	Reference temperature at which oxidation rates were measured, °C
261	KOX2O(1,1)	Second-order, 20°C oxidation rate constant for dissolved chemical, L/mole-day
266	KOX2O(2,1)	Second-order, 20°C oxidation rate constant for DOC-bound chemical, L/mole-day
271	KOX2O(3,1)	Second-order, 20°C oxidation rate constant for particulate chemical, L/mole-day
276	EOX(1)	Activation energy for oxidation, kcal/mole

Table 2.10. Biodegradation constants.

Constant	Variable	Definition
602	XBIO	Biodegradation Option 0 = No biodegradation 1 = Biodegradation occurs
146	KBIO20(1,1)	Second-order 20°C biodegradation rate constant for dissolved chemical, mL/cells-day
151	KBIO20(2,1)	Second-order 20°C biodegradation rate constant for DOC-bound chemical, mL/cells-day
156	KBIO20(3,1)	Second-order 20°C biodegradation rate constant for particulate chemical, mL/cells-day
161	Q10DIS(1)	Temperature correction factor for dissolved chemical biodegradation; multiplication factor for 10°C temperature increase
166	Q10DOC(1)	Temperature correction factor for DOC-bound chemical biodegradation; multiplication factor for 10°C temperature increase
171	Q10PAR(1)	Temperature correction factor for particulate chemical biodegradation; multiplication factor for 10°C temperature increase

Table 2.11. Volatilization constants.

Constant	Variable	Definition
136	XVL	Volatilization option for liquid phase mass transfer: 0 = no volatilization 1 = Owens 2 = Modified O'Connor-Dobbins 3 = Churchill 4 = O'Connor "short" form 5 = Mackay 6 = Reaeration rate input by user and converted to a liquid phase mass transfer rate 7 = Volatilization rate directly input by user 8 = O'Connor "long" form
2	XVG	Volatilization option for gas phase mass transfer: 0 = No gas phase resistance/no volatilization (default if XVL=0) 1 = O'Connor-Rathbun 2 = Mills et al. 3 = O'Connor 4 = Mackay 5 = Ambrose et al. for flowing systems 6 = Mackay still-air 7 = Liss
1	XVH	Henry's Law constant option: 0 = HLC is a chemical constant (default if XVL=0) 1 = Direct expression of temperature 2 = Calculated from temperature-dependent vapor pressure and solubility
137	HLC25	Henry's Law constant at 25°C, atm-m3/mole
600	HLCA0	Henry's Law constant temperature factor a_0, dimensionless. Used in temperature-based HLC estimation expression: $\ln H = a_0 - \frac{a_1}{T + 273.15}$

Table 2.11 (continued). Volatilization constants.

Constant	Variable	Definition
601	HLCA1	Henry's Law constant temperature factor a_1, dimensionless
138	KLT	Volatilization temperature correction factor, dimensionless
139	KVOG	Measured ratio of volatilization to reaeration rates
5	AIRTMP	Multiplier for air temperature time function, °C or normalized (dimensionless)
8	ATMOS	Atmospheric concentration of chemical, µg/L

Table 2.12. "Extra reaction" constants.

Constant	Variable	Definition
605	XERXN	Extra Reaction Option: 0 = No extra reaction 1 = Extra reaction occurs
573	TREFE	Reference temperature at which extra reaction rates were measured, °C
576	KE2O(1,1)	Second-order, 20°C extra reaction rate constant for dissolved chemical, 1/[E]-day
581	KE2O(2,1)	Second-order, 20°C extra reaction rate constant for DOC-bound chemical, 1/[E]-day
586	KE2O(3,1)	Second-order, 20°C extra reaction rate constant for particulate chemical, 1/[E]-day
591	EEX(1)	Activation energy for extra reaction, kcal/mole

constants specified in Data Group H are coupled with the parameters in Data Group G and time functions in Data Group I to permit simultaneous spatial and temporal variation of chemical-specific equilibria and reactions.

There are many possible combinations of constants, parameters, and time functions that can be specified to represent simulated equilibria or kinetics. As a result it is not possible to enumerate every possible option for using each constant. However, the definitions and use of the range of constants in IPX is consistent with typical environmental engineering usage as described in references texts such as those by Thomann and Mueller (1987) and Chapra and Reckhow (1983), and Chapter 1 of this manual. However, users are strongly advised to review the IPX source code as well as Tables 2.3-2.12 to ensure that constants for desired equilibria and reactions are properly specified. With this caveat in mind, a brief overview of commonly used constants follows.

At equilibrium level 1, it is only necessary to also input a partition coefficient to represent partitioning to each sorbing solids class using PIXC (constants 111, 116, and 121). For equilibrium level 2, in addition to specifying PIXC, the user may use Data Group G parameters numbers 6-9 and Data Group I time functions 19-21 to permit spatial and temporal variation of partition coefficients; at this level, the parameters and time function should be treated as spatial and temporal, dimensionless scale factors of PIXC. At equilibrium level 3, the user must specify LKOC (constant 101), or other constants required to approximate LKOC, and enter the FOC-related parameters and time functions in Data Groups G and I. At equilibrium level 4, the user must specify NUX (constant 106) in addition to those inputs required for equilibrium level 3.

As previously noted, it is difficult to enumerate all possible options for specifying constants. Although this is particularly true for representing chemical reaction kinetics, some general guidelines are provided. At kinetic level 1, reaction rates are constant and can be entered as either reaction half-life ($t_{1/2}$) or rate constants (K_i). Reaction half-life or rates for each chemical may be specified for each relevant process (hydrolysis, oxidation, biodegradation, volatilization, photolysis, or user-defined) or lumped into a single "decay" constant. In general, it is preferable to specify reaction rates for each relevant reaction pathway individually. At kinetic level 2, reaction rates can be spatially and temporally varied through the use of Data Group G parameters and Data Group I time functions. At kinetics level 3, reaction kinetics are "second-order" and can depend on some characteristic of the water body (such as ozone or bacterial concentrations) in addition to the specified reaction rate constant (which itself can be spatially and temporally variable). Reactions need not be second-order to be simulated. For

example, consider a simple oxidation reaction; if the concentration of the oxidant is constant, it could be "lumped" with the rate constant and represented as an overall "first-order" reaction. At kinetic level 4, reaction transformation products are simulated and yield coefficients for each relevant transformation process must be specified.

To specify volatilization, the user must generally choose both a liquid and gas phase resistance option, and a Henry's Law Constant option. If XVL is specified but XVG is not, the gas phase resistance defaults to zero when computing the overall volatilization rate. If XVG is specified but XVL is not, XVL has a default value of zero and no volatilization is computed for the chemical. If XVH is not specified, then HLC will be treated as a constant, either specified by input of HLC25 or calculated from VAPRG and SOLG. The user is reminded to verify that the volatilization options specified are appropriate for the range of environmental conditions encountered. Liquid and gas phase mass transfer options are described in Table 2.11. Some caveats regarding the selection of volatilization options in conjunction with parameter and time function requirements follow.

To use XVG options 1-5 and 8, the user must specify both WINDN, time function 9 in Data Group I, and WVEL, parameter 4 in Data Group G of the input data set. The variable SWIND is the product of WVEL and WINDN and is used for XVG options 1-4 and 7 (SWIND is used to compute USTAR for options 3, 4, and 7). The default value for WVEL is zero and the default for WINDN is 1. Unless both values are specified, SWIND will have a value of zero.

The use of REARN, time function 12 in Data Group I, and REAR, parameter 5 in Data Group G of the input data set, depend on the XVL option chosen. For XVL options 1-5 and 8, REARN does not directly enter into the volatilization computations but is used to control whether volatilization occurs or not. For XVL options 6-7, the internally computed variable SREAER, defined as the product of REARN and REAR, enters directly into the computations.

For XVL options 1-5 and 8, REARN is used to toggle the volatilization computation on or off to represent conditions such as ice cover. To use REARN as a toggle, the user should specify a value of 1 (any non-zero value will work) for ice free periods and zero for periods of ice cover. No volatilization is computed for any period when the value of REARN is zero. The default value of REARN is 1. So, if REARN is not specified for XVL options 1-5 and 8, volatilization computations will always be computed (ice free conditions). The parameter REAR does not need to be specified for XVL options 1-5 and 8.

For XVL option 6, the use of REARN depends on the value specified for KVOG. If KVOG is specified as a chemical-specific reaeration rate or liquid phase mass transfer coefficient, REARN is a dimensionless time function through which the reaeration rate is varied with time. If KVOG is given a value of 1, REARN is a time series of reaeration/mass transfer coefficients (units in m/day). The user should note that if REARN is used to specify a time series of mass transfer coefficients, the same coefficient value will be applied to all chemicals volatilizing. For either case, REAR is a segment-specific normalization constant through which the liquid phase mass transfer coefficient can be varied segment by segment. The default value of REARN is 1. So, if REARN is not specified the liquid mass transfer coefficient will not vary with time. The parameter REAR must be specified for this option. The default value of REAR is zero. So, if REAR is not specified the value of SREAER and the resultant liquid phase mass transfer coefficient will be zero and a divide by zero error will occur.

For XVL option 7, the use of REARN depends on the value specified for KVOG. If KVOG is specified as a chemical-specific volatilization rate, REARN is a dimensionless time function through which the volatilization is varied with time. If KVOG is given a value of 1, REARN is a time series of volatilization rates (units in m/sec). The user should note that if REARN is used to specify a time series of volatilization rates, the same rate will be applied to all chemicals volatilizing. For either case, REAR is a segment-specific normalization constant through which the volatilization rate can be varied segment by segment. The default value of REARN is 1. So, if REARN is not specified the volatilization rate will not vary with time. The parameter REAR must be specified for this option. The default value of REAR is zero. So, if REAR is not specified the value of SREAER and the resultant volatilization rate will be zero and no volatilization will occur.

Potentially all volatilization options and rates depend on temperature. Specifically, the contaminant diffusivity in water and air, air-water partition coefficient (including the Henry's Law constant), and the density and viscosity of water and air are functions of temperature. To account for temperature variation in volatilization, the water and air temperature must be specified.

The water temperature, TMP, is internally computed as the product of a water temperature time function TEMPN(1-4), time functions 1-4 in Data Group I, TMPFN, and TEMP, parameters 2 and 3 in Data Group I. Up to four different water temperature time functions can be specified. Unless environmental conditions suggest otherwise, it is generally not necessary to specify more than one water temperature time function. TMPFN is a pointer

that indicates which time function (1-4) is used to compute water temperature for a given segment. TEMP is a segment-specific normalization constant through which the water temperature for a given time function can be varied segment by segment. The default value of TEMP is zero and the defaults of TMPFN and TEMPN are 1. So, unless all three values are specified, TMP will have a value of 0°C (273.15 K).

The air temperature, ATMP, is internally computed as the product of AIRTMPN, time function 13 in Data Group I, and AIRTMP, constant 5 in Data Group H of the input data set. The default value of AIRTMP is zero and the default of AIRTMPN is 1. So, unless both values are specified, ATMP will have a value of 0°C (273.15 K).

Due to the large number of possible XVL and XVG combinations, it is not feasible to specifically list every possible combination or use of volatilization options that may require specification of the water and/or air temperature. The user is advised to examine the IPX source code to confirm whether specification of the water and/or air temperature is required for the volatilization options chosen.

2.3.3 Kinetic Time Functions: Data Group I

The 21 kinetic time functions the user can specify are listed in Table 2.13. These time functions permit the user to temporally vary the environmental properties that control the rates at which simulated chemicals react. The user need only specify those functions required to represent the particular reactions simulated. It is not necessary to specify any time functions unless required to represent a specific mass transport pathway. The parameters specified in Data Group G are coupled with the time functions in Data Group I to permit simultaneous spatial and temporal variation of simulation conditions.

For simple simulations, no time functions need be specified. For simulations in which contaminants are transferred between media (air-water, water-sediment) or react at variable rates, time functions for each relevant process may be specified. TEMPN can affect all reactions. Volatilization may require VELN(1-4), REARN, WINDN and AIRTMPN. Photolysis may require PHTON. Hydrolysis may require PHNW and PHNS. Biodegradation may require BACNW and BACNS. Values for functions not specified default to 1.0.

Table 2.13. Data Group I kinetic time functions.

ISC	ANAME(ISC)	VALT(ISC)
1	TEMPN(1)	Water temperature function 1. Values for functions TMPN(1-4) can be either normalized (dimensionless) or actual temperatures in °C, depending upon the use of parameter TEMP(ISEG) specified in Data Group G.
2	TEMPN(2)	Water temperature function 2, normalized or °C.
3	TEMPN(3)	Water temperature function 3, normalized or °C.
4	TEMPN(4)	Water temperature function 4, normalized or °C.
5	VELN(1)	Water velocity function 1, m/sec. The velocities input through functions VELN(1-4) are added to the net water velocities VELOCG(ISEG) computed from flow and the hydraulic parameters specified in Data Group C.
6	VELN(2)	Water velocity function 2, m/sec.
7	VELN(3)	Water velocity function 3, m/sec.
8	VELN(4)	Water velocity function 4, m/sec.
9	WINDN	Wind velocity function, m/sec. This time function is multiplied by the segment specific wind parameter WVEL(ISEG) specified in Data Group G.
10	PHNW	Water column pH function; pH units or dimensionless (normalized). This function is multiplied by the segment specific pH parameter, PH(ISEG), entered in Data Group G.
11	PHNS	Benthic pH function; pH units or normalized (dimensionless). This function is multiplied by the segment pH parameter, PH(ISEG), for benthic segments.
12	REARN	Reaeration coefficient, day^{-1} or normalized. This function is multiplied by the segment specific reaeration parameter REAR(ISEG) entered in the Data Group G.

Table 2.13 (continued). Data Group I kinetic time functions.

ISC	ANAME(ISC)	VALT(ISC)
13	AIRTMPN	Air temperature, °C or normalized. Used for computing reaeration/volatilization.
14	CHLN	Phytoplankton chlorophyll concentration, mg/L. This variable is multiplied by the segment specific chlorophyll parameter CHPHL(ISEG) entered in Data Group G.
15	PHTON	Normalized light intensity, dimensionless. This is used for photolysis option 2 to adjust the measured rate constant under controlled light intensity to a predicted rate constant under ambient light intensity.
16	BACNW	Time variable bacteria concentration in the water column, mg/L. This is multiplied by the segment specific parameter BAC entered in the parameter section.
17	BACNS	Normalized benthic bacteria function, dimensionless. This is multiplied by the segment bacteria parameter BAC(ISEG) for benthic segments.
18	ATCHEM	Normalized atmospheric chemical concentration function, dimensionless. This is multiplied by the atmospheric chemical concentration constant ATMOS for each chemical.
19	MFOC(1)	Time variable fraction organic carbon content for solids type 1 in the water column. This is multiplied by the segment f_{oc} parameter FOC(ISEG,1). Applies to the water column only.
20	MFOC(2)	Time variable fraction organic carbon content for solids type 2 in the water column. This is multiplied by the segment f_{oc} parameter FOC(ISEG,2). Applies to the water column only.
21	MFOC(3)	Time variable fraction organic carbon content for solids type 3 in the water column. This is multiplied by the segment f_{oc} parameter FOC(ISEG,3). Applies to the water column only.

CHAPTER 3

IPX SIMULATION OUTPUT AND POST-PROCESSING

3.1 IPX OUTPUT OVERVIEW

IPX produces four output files that hold a variety of simulation results. These files use the root file name of the input data file with a unique identifying extension. The most important of these is the *.DMP file (where * is the root name of the input data file), a direct access file that contains all kinetic display variables for each state variable for each model segment at each print interval throughout the simulation. Other files created by an IPX simulation include *.DMA, *.EXP, *.MSB, and *.RST, *.OUT.

3.2 THE *.DMP FILE

The *.DMP file is a direct-access file in which instantaneous (point-in-time) simulation results are stored. Results are stored for all water column and sediment segments as well as all elements in the ghost stack (if any). The results stored in this direct access file can be retrieved with the W4DIS274 post-processing program. The W4DIS274 program prompts the user to input desired display options and creates a sequential-access (ASCII text) file that contains the specified simulation results. Display options for solids include the total solids concentration and the concentration of each solids type. Display options for chemicals include the total (sum of all phases) chemical concentration, the dissolved, DOC-bound, and particulate concentrations of each chemical on a mass per volume basis, and the particulate chemical concentration on a mass per mass basis. Descriptions of the W4DIS274 post-processing program and the available display options are presented in Section 3.8.

3.3 THE *.DMA FILE

The *.DMA file is a direct-access file in which time averaged simulation results are stored. Results are stored for all water column and sediment segments. No results for the sediment ghost stack are stored in the *.DMA file. The results stored in this direct access file can be retrieved with the W4DIS274 post-processing program. The process for retrieving simulation results from the *.DMA file using the W4DIS274 post-processor are identical to the process used for the *.DMP file.

3.4 THE *.EXP FILE

The *.EXP file is a sequential-access file that contains the times series of simulated export for total solids and any one additional state variable (solid or chemical) defined in Data Group A. Export is the mass transported by advection and dispersion across the system interface defined in Data Group A. The values displayed on each line of the *.EXP file are the cumulative masses exported across the defined interface since the previous print interval.

3.5 THE *.MSB FILE

The *.MSB file contains a mass balance record for all state variables (solid or chemical) simulated. The mass balance is computed for all segments in the model network over the entire simulation period. In this file, the accumulated masses transported into and out of each model segment by each fate pathway are reported in kilograms. The fate pathways include loading, advection, dispersion, pore water transport, settling (in), resuspension (in), burial (out), scour (out), biodegradation, hydrolysis, oxidation, photolysis, and volatilization. Also reported are the total resident mass in each segment and the estimated residual (unaccounted for) mass. In addition, a report of final conditions in the sediment ghost stack is reported element by element for each sediment stack. Reported conditions include: ghost volume, surface area, thickness, elevation within the sediment bed, and the concentration of each state variable.

3.6 THE *.OUT FILE

The *.OUT file contains an “echo” of all information in the model input data file and a record of any input data structure or simulation errors. As an input file is read at the start of an IPX simulation, all model input data are written to the *.OUT file. If any input data file structure errors are found at the time the input file is read, model execution stops and a message is written to the *.OUT file at the point where the error was discovered. IPX input data files can be very long and difficult to read; the *.OUT file provides a simple means for the user to confirm that all input data are correctly read by IPX. If conditions become unstable during a simulation, model execution stops and an error message is written to the *.OUT file. However, the user should be aware that IPX does “trap” arithmetic faults such as division by zero errors; arithmetic faults that cause simulation execution to abort may not be reported.

3.7 THE *.RST FILE

The *.RST file contains a “snapshot” of the volume and concentrations of each system in every model segment. Writing data to and/or reading data from the *.RST file is controlled

through the variable ICFL that is input in Data Group A of the input file. Values are written to the *.RST file every TRST days and at the end of the simulation, replacing (overwriting) any previous values (if any) stored in the file. This file can be read by IPX to conduct a continuous series of simulations or resume a long simulation simulation that did not complete.

3.8 W4DIS274: THE *.DMP AND *.DMA FILE POST-PROCESSOR

The W4DIS274 post-processing program is used to retrieve simulation output from the direct-access *.DMP and *.DMA files. Display variables for water column and sediment segment retrievals are listed in Table 3.1. Display variables for sediment archive stack retrievals are listed in Table 3.2. The sediment archive stack is defined below. The results of W4DIS274 retrievals are stored in a tab-delimited, ASCII text format in a file with the default name *.TBL.

To retrieve output for water column and sediment segments, the user must differentiate between chemical-independent and chemical-dependent display variables. Display variables 1-7 (include solids concentrations, segment volume, segment depth, and segment type) are chemical-independent. Display variables 8-19 are chemical-dependent.

When prompted for a display option list, the user must precede each chemical-dependent display variable number with the chemical number and a colon (:). For convenience, ranges of chemicals, display variables, and segment numbers can be specified using square brackets ([,]) and colons (:). For clarity, four examples follow:

Example 1 - Specifying chemical-independent and chemical-dependent display variables.

1. Total Solid
2. Solid 1
3. Solid 2
4. Solid 3
5. Segment Volu
6. Segment Dpth
7. Segment Type
8. Total Chm
9. Dis. Chm
10. Doc Chm
11. Part Chm
12. Part Chms
13. Ionic Chm
14. Biodeg Chm
15. Hydrol Chm
16. Photl Chm
17. Volat Chm
18. Oxid Chm
19. Xtra Chm

Enter display variable list -> 1, 5, 6, 1:8, 2:8

Table 3.1. W4DIS274 display variables.

Number	Display Variable	Definition
1	Total Solid	Total solids concentration, mg/L
2	Solid 1	Solids type 1 concentration, mg/L
3	Solid 2	Solids type 2 concentration, mg/L
4	Solid 3	Solids type 3 concentration, mg/L
5	Segment Volume	Segment volume, m^3
6	Segment Depth	Segment depth (thickness), m
7	Segment Type	Segment type (1, 2, 3, 4, 5, or 6)
8	Total Chm	Total chemical concentration, µg/L
9	Dis. Chm	Dissolved chemical concentration, µg/L
10	Doc Chm	DOC-bound chemical concentration, µg/L
11	Part Chm	Particulate chemical concentration, µg/L
12	Part ChmS	Particulate chemical concentration on a mass basis, $\mu g/kg_{total\ solids}$
13	Ionic Chem	Total ionic chemical concentration, µg/L
14	Biodeg Chm	Biodegradation rate constant, day^{-1}
15	Hydrol Chm	Total hydrolysis rate constant, day^{-1}
16	Photl Chm	Photolysis rate constant, day^{-1}
17	Volat Chm	Volatilization rate constant, day^{-1}
18	Oxid Chm	Oxidation rate constant, day^{-1}
19	Xtra Chm	Extra rate constant, day^{-1}

This example input will select total solids, segment volume, segment depth, total concentration of chemical 1 and total concentration of chemical 2.

Example 2 - Specifying ranges of chemical-dependent display variables with the [ ] and : separators.

Enter display variable list -> 1,[1:3]:8,4:[9:12]

This example will select total solids, total chemical concentration for chemicals 1, 2, and 3, and dissolved, DOC-bound, particulate and sorbed particulate concentrations for chemical 4.

Example 3 - Specifying ranges of chemical-dependent display variables with the [ ] and : separators.

Enter display variable list-> [l:10]:[8:19]

This example will select all chemical-dependent display variables [8:19] for chemicals 1 through 10 [1:10].

Example 4 - Specifying ranges of segments with the [ ] and : separators.

Enter in segment numbers -> 1,2,3,[10:17]

This example will select segments 1, 2, 3, 10, 11, 12, 13, 14, 15, 16 and 17.

The sediment stack archive is a report of conditions for each sediment stack including the surficial sediment segment, all specified subsurface sediment segments, and all ghost elements in a stack. As data are retrieved, each element in the archive stack is assigned a layer number according to its vertical position above the stack bottom. The bottom-most element of the stack is assigned the largest possible layer number value. Each layer above that is assigned the next largest layer number. This process continues until all ghost stack and subsurface sediment layers are assigned a layer number. Unoccupied elements of the sediment stack will appear as zeros (nulls) over all occupied stack elements. The surficial sediment segment is always assigned a layer number of zero (0). Users should be aware that unoccupied stack elements will appear as empty layers between the last occupied ghost/subsurface sediment element and the surficial sediment element. Empty layers contribute zero to the total elevation of the sediment stack. If the surface sediment element is unoccupied, this indicates that no sediment is present. If any sediment is present at a location, at least the surficial sediment element of the stack (Layer 0) will be occupied.

Retrieving output for the sediment stack archive follows procedures similar to those used for the water and sediment column. To reach the menu for archive stack retrievals, the user must select Option 5 from the main menu. To retrieve output from the archive stack, the user must again differentiate between chemical-independent and chemical-dependent display variables. Display variables 1-8 (element volume, surface area, thickness, and solids concentrations) are chemical-independent. Display variable 9 is chemical-dependent. When prompted for a display option list, the user must precede each chemical-dependent display variable number with the

Table 3.2. W4DIS274 sediment archive stack display variables.

Number	Display Variable	Definition
1	Volume	Volume of stack element, m^3
2	Surface Area	Surface area of stack element, m^2
3	Thickness	Thickness (depth) of stack element, m
4	Elevation	Distance from the bottom of the sediment stack to the top of the layer, m
5	Total Solid	Total solids concentration, mg/L
6	Solid 1	Solids type 1 concentration, mg/L
7	Solid 2	Solids type 2 concentration, mg/L
8	Solid 3	Solids type 3 concentration, mg/L
9	Total Chm	Total chemical concentration, µg/L

chemical number and a colon (:). As previously described, ranges of chemicals, display variables, and segment numbers can be specified using square brackets ([,]) and colons (:).

CHAPTER 4

IPX INPUT DATA FILE PRE-PROCESSING

4.1 IPX Input Data File Pre-Processing Program Overview

A difficult but critical aspect of developing a water quality model for any river is to estimate settling and resuspension velocities for each solids type simulated. Four input data pre-processing programs are provided to help simplify this task: REDUCE, SETTLE, RESUSPND, and TIMESTEP. These pre-processing programs are designed to help the user define model inputs for the simulation hydrograph and also settling and resuspension velocities and numerical integration time-steps as a function of the hydrograph. A description of each pre-processing program follows. However, the user is advised to examine the FORTRAN source code for these programs to fully understand their proper operation and capabilities.

4.2 REDUCE: The Simulation Hydrograph Pre-Processor

Flow data are available through a number of resources. Of particular note is the USGS flow file portion of the USEPA's STORET database. Daily flows for many streams are available from this data source. The REDUCE pre-processing program reads a user-provided input file (from STORET for example) that may contain years of daily flow observations for a stream and produces a file that can be used as input for Data Group D of the IPX framework. The maximum number of data points that can be used to define time series inputs in IPX is controlled by the value of the FORTRAN parameter MB in the file WASP_IPX.CMN and is ultimately constrained by available computer memory. It is often desirable, and sometimes necessary due to the memory limitations, to reduce the number of data points that define the simulation hydrograph. For example, using daily observations, the hydrograph for a 25 year simulation would be defined by 9125 points. It is sometimes undesirable to develop model inputs based on such a large number of data points. This pre-processing program reduces the number of points used to define the simulation hydrograph by eliminating those values that do not differ significantly from the previous value. This procedure permits the user to manage the size of the simulation hydrograph as well as settling and resuspension velocities and numerical integration time-steps.

When using REDUCE, the user is interactively prompted for information that controls how the program develops the simulation hydrograph. The first prompt requests the name of the data file that contains the flow data. Input files for the REDUCE pre-processor should typically be of the form *.PRE_HYDRO. It is important that the user consistently organize the input file such that all flow observations for each year are in a column; each column (representing one year of flow data) must have 365 rows (one row for each day of the year). For example if Day 1 of the simulation is January 1, the value representing January 1 of the second year of simulation will be in the first row of the second column. The second prompt requests the number of years for which flow data are input. The remaining prompts request information used to reduce the number of flow values that define the hydrograph. Although REDUCE can be used independent of the units (ft^3/s, m^3/s) of the flow values, units of m^3/s are recommended due to the input requirements of the SETTLE and RESUSPND pre-processing programs.

The next two prompts request that the user specify thresholds that divide the input flows into three classifications: high, medium, and low flows. The remaining prompts request that the user specify tolerance levels for each flow classification. The tolerance levels are fractions ($0 <$ tolerance < 1) that are used to assess whether a flow value is sufficiently similar to neighboring flow values that it need not be included as a time-break in the simulation hydrograph. After reading a flow value from the *.PRE_HYDRO file, the program determines whether to include the value as a time-point in the simulation hydrograph by comparing it to the preceding flow value selected as a time-break. If the current flow value is within the tolerance (previous value*(1 - tolerance) < current value < previous value*(1+tolerance)), then it is not included as a time-break in the simulation hydrograph. If the flow value is outside this range, then it is included in the simulation hydrograph as a time-break. This process in repeated for each input flow value. However, the last value input is always included as a time-break to insure proper operation of the IPX framework.

Output from the REDUCE pre-processor is contained in a file named *.POST_HYDRO. The number of time-breaks, k, in the simulation hydrograph is given on line 1 of the output file (i5 format), followed by k lines of paired values that are the simulation time (in days) and flow defining the hydrograph (i5,a1,e11.4 format). The simulation hydrograph defined in the *.POST_HYDRO file can be used as input to estimate settling and resuspension velocities, numerical integration time-steps, as well as input for IPX Data Group D after simple formatting.

4.3 SETTLE: The Settling Velocity Pre-Processor

The SETTLE pre-processor is used to estimate TSS settling velocities as a function of the simulation hydrograph when simulating all solids as a single state variable (TSS). SETTLE estimates the distribution of particle into three categories: fine, medium, and coarse. Particles within each category are assigned a settling velocity. An overall TSS settling for each time-break in the hydrograph is computed as the sum of the products of the fraction of particles in each category and settling velocity of the particle category.

When using SETTLE, the user is interactively prompted for the name of the data file that contains the hydrograph (from REDUCE) and settling velocities of the three particle categories at each simulation time-break. All other information necessary to control how settling velocities are estimated is read directly from the input file. Input files for the SETTLE pre-processor should typically be of the form *.PRE_VS. The first line of the input file must specify whether flows in the river system are controlled or uncontrolled (0 represents a controlled system, 1 represents an uncontrolled system). The user must then provide information describing the frequency distribution of river flows. For controlled rivers, the user must specify the river flow at the 50^{th}, 70^{th}, 80^{th}, and 98^{th} percentile in m^3/s, each on a separate line. For uncontrolled systems, the user must specify the river flow at the 80^{th}, 98^{th}, and 99.9^{th} percentile in m^3/s, each on a separate line. The remainder of the file must be organized such that the simulation time, flow, fine particle and settling velocities for the fine, medium, and coarse particle categories appear on a single line for each time-break in the hydrograph. All flows must be in m^3/s. All settling velocities must be in m/s. All times must be in days (recall that all time output from REDUCE is in days). SETTLE then calculates the fraction of fine, medium and coarse particles in the water column at that time based on the flow-rate. These fractions are then used to calculate the average settling speed for all particles based on the three input settling speeds.

Output from the SETTLE pre-processor is contained in two files. The first file is named *.POST_VS. This file has k lines, where k is the number of time-breaks in the simulation hydrograph. Each line contains the fraction of particles that are fine, medium, and coarse (the sum of these fractions will be 1), the computed overall TSS settling velocity, and the simulation time. The second file is named *.VS. This file includes the number of entries, k, on the first line, followed by k pairs of TSS settling velocity and simulation time values. After the first line, each line of the *.VS file will have up to four pairs of entries per line and will have as many lines as are needed for k pairs of settling velocities and simulation times (4(e10.2,f10.0) format). This file can be used as input for IPX Data Group D without additional formatting.

4.4 RESUSPND: The Resuspension Velocity Pre-Processor

The RESUSPND pre-processor is used to estimate resuspension velocities as a function of the simulation hydrograph, the time history of resuspension events, and sediment armoring. RESUSPND estimates the shear stress exerted by water flowing over the sediment bed from which the mass of sediment resuspended during an event is computed. A resuspension velocity for each time-break in the hydrograph is then computed from the mass resuspended as a function of the sediment bulk density.

When using RESUPEND, the user is interactively prompted for the name of the data file that contains the hydrograph (from REDUCE) and settling velocities of the three particle categories at each simulation time-break. All other information necessary to control how resuspension velocities are estimated is read directly from the input file. Input files for the RESUSPND pre-processor should typically be of the form *.PRE_VR. The first line of the input file must specify the sediment properties that control resuspension (as described in Section 1.4.5.2.): taucrit, A0, m, Ax, density, te, and NCFLG. The first three constants (taucrit, A0, m) are parameters in the epsilon (ε) equation (Equation 1.25.). The next constant (Ax) is a parameter in the shear stress equation (Equation 1.26.). The shear stress equation relates stream flow to the shear exerted at the sediment-water interface. The next two constants (density and te) are parameters used to express the mass of sediment resuspended as a resuspension velocity (Equation 1.27.). The last constant (NCFLG) indicates whether the sediment bed experiences non-cohesive resuspension (0 indicates that non-cohesive resuspension does not occur, 1 indicates that non-cohesive resuspension does occur). The epsilon equation defines the total mass of cohesive sediment that can be resuspended for a given stress applied at the sediment-water interface. In general, once the mass of sediment resuspended during an event equals epsilon, resuspension decreases to background levels. However, non-cohesive sediments (such as coarse sands) do not armor and will continue to resuspend as long as shear stress exerted at the sediment water interface exceeds the critical shear of the non-cohesive sediments. If NCFLG = 1, the second line of the input file must specify taucrit_nc, the critical shear stress for resuspending non-cohesive sediment, in dynes/cm^2. The remainder of the input file must be organized such that the simulation time, flow, the sediment age factor of the surficial age layer (Z), and the background resuspension velocity appear on a single line for each time-break in the hydrograph. All flows must be in m^3/s. All background resuspension velocities must be in m/s. All times must be in days (recall that all time output from REDUCE is in days). RESUSPND then calculates the resuspension velocity at each time, based on the flow-rate and the computed time history of sediment erosion potentials.

Output from the RESUSPND pre-processor is contained in two files. The first file is named *.POST_VR. This file has k lines, where k is the number of time-breaks in the simulation hydrograph. Each line contains the value of epsilon for the given flow-rate, the depth of sediments resuspended, the event resuspension velocity (does not include background resuspension), the overall resuspension velocity (includes background resuspension), and the simulation time. The second file is named *.VR. This file includes the number of entries, k, on the first line of the file, followed by k pairs of resuspension velocity and simulation time values. After the first line, each line of the *.VR file will have up to four pairs of entries per line and will have as many lines as are needed for k pairs of resuspension velocities and simulation times (4(e10.2,f10.0) format). This file can be used as input for IPX Data Group D without additional formatting.

4.5 TIMESTEP: The Simulation Time-Step Pre-Processor

The TIMESTEP pre-processor is used to estimate the optimum model time-step as a function of the simulation hydrograph and volume of the limiting (critical) segment in the model network. TIMESTEP estimates the hydraulic residence time (HRT) from the critical volume and flow. A suggested time-step history for the given hydrograph is then computed.

When using TIMESTEP, the user is first interactively prompted for the volume of the critical segment in the model network. Next, the user is prompted for a hydraulic residence time divisor factor (HRTDF). Finally, the user is prompted for the name of the data file that contains the hydrograph (from REDUCE). For advectively dominated tributary systems, the critical model segment will typically be the smallest water column segment in the network. The HRTDF is used as a "safety" factor, to ensure that the computed model time-steps do not exceed the maximum stability criterion for the numerical integration approach IPX uses to solve the mass balance equation. HRTDFs will typically have a value of 3.0. However, users should be aware that IPX treats model time-steps as a step, rather than a linear, function so it may be necessary to use a larger factor during rapidly changing portions of the hydrograph. Input files for the TIMESTEP pre-processor should typically be of the form *.PRE_DT. The input file must be organized such that the simulation time and flow appear on a single line for each time-break in the hydrograph. TIMESTEP will read all lines from the input file until the end of the file is reached.

Output from the TIMESTEP pre-processor is contained in two files. The first file is named *.POST_DT. This file has k lines, where k is the number of time-breaks in the simulation hydrograph. Each line contains the minimum hydraulic residence time, the maximum model time-step, the "suggested", model time-step, and the simulation time. The second file is named *.DT. This file includes the number of entries, k, on the first line of the file, followed by k pairs of time-step and simulation time values. After the first line, each line of the *.DT file will have up to four pairs of entries per line and will have as many lines as are needed for k pairs of time-steps and simulation times (4(e10.2,f10.0) format). This file can be used as input for IPX Data Group A without additional formatting.

CHAPTER 5

IPX PROGRAMMER'S GUIDE

5.1 IPX PROGRAMMING OVERVIEW

This chapter provides a brief overview of the important programming aspects of the IPX framework. In addition to its inherent flexibility, one demonstrable strength of IPX and its WASP4 predecessor is that, with a basic degree of familiarity, users can customize most functions of the framework to create highly specialized applications to address a broad range of water quality simulation issues. However, a word of caution is in order: many users assume that there are no errors in "official" software distributed or supported by USEPA. IPX, like WASP4 and its antecedents, is a complex program. No guarantees are made regarding either the suitability of IPX for constructing a water quality model or the computational performance of the code. Although substantial efforts have been taken to examine all aspects of the code, the user is strongly advised to carefully examine both the IPX source code and all model outputs to ensure proper operation.

The authors would appreciate receiving notification of any problems encountered with the IPX program. This may be done by mail, phone, or email to:

Mark Velleux, Wisconsin Department of Natural Resources WT/2, P.O. Box 7921, Madison, Wisconsin 53707-7921; Phone (608) 267-5262; email: vellem@dnr.state.wi.us.

5.2 AVAILABILITY OF IPX PROGRAMS AND PORTING TO OTHER PLATFORMS

The IPX programs, and this User's Guide, will be provided upon request to the authors. IPX is not officially supported by either the USEPA or WDNR. This means that users should not expect support beyond receiving the programs and User's Guide, unless special arrangements are made with USEPA or WDNR.

IPX and its supporting suite of pre- and post-programs were initially developed in FORTRAN77 in a VAX/VMS environment. When porting the IPX source code to other environments, users should be aware that many VAX FORTRAN programming conventions (such as the treatment of uninitialized or undeclared variables, etc.) were used. Many compilers have options to accommodate VAX conventions and VAX FORTRAN extensions. These options should be used to help ensure that IPX operates consistently on all platforms to which it is ported. IPX has been successfully ported to Sun (Solaris) and Compaq/DEC Alpha (Digital UNIX, OSF/1) UNIX workstations. IPX has also been successfully ported to Cray YMP and C90 supercomputers as well as LINUX-based and Windows NT-based personal computers.

5.3 UNIX ENVIRONMENT DEVELOPMENT TOOLS FOR IPX

Following its first release, the IPX program source code was ported to a UNIX computing environment to facilitate development efforts. Three basic modifications were made at the time the source code was ported. The first modification was splitting the program source code into a separate file for each subprogram unit (subroutine). The second modification was implementation of the UNIX C preprocessor utility *cpp* to allow flexible inclusion of the platform-dependent codes used by different computer operating systems (i.e. VMS, OSF/1, Solaris, etc.). The third modification was implementation of a UNIX *Makefile* to provide swift and organized compilation and loading of the IPX source code.

The IPX source code is now contained in over seventy FORTRAN source files containing the IPX subprograms and include files. Files that contain source code for the IPX subprograms are identified by the file extension ".F". Files that contain included common blocks are identified by the file extension ".inc". Other files include the message file *messfile_r1.dat* (needed during program execution), the *platform.h* file (used to define platform specific conditions for source code compilation), and the UNIX *Makefile* (used to manage source code compilation).

UNIX *cpp* is a program run prior to compilation of program source code that reads the source, interprets specially prepared directives imbedded in it, and outputs another version of the source whose modifications are determined by the *cpp* directives and predefined variables named *cpp macros* that are used both as flags to steer execution of the preprocessor and as symbols representing some syntax of the program. These symbols can be defined either within the source code file of the program itself, or in an independent file made known to *cpp* at the time that the preprocessing occurs. (Such symbols can also be defined at compile time, but instances of this

practice are more the exception than the rule and are not currently being used as a part of IPX development.) The current implementation of IPX uses a file named *platform.h* to define *cpp* macro flags. A copy of this file is provided in the Appendix, together with a description of the individual flags currently being used. A simple example demonstrating the use of *cpp* is shown below:

```
#define    FLAG   1
      PROGRAM MESSAGE
*
#if (FLAG)
      PRINT *, 'This message is only printed if FLAG is set'.
#endif
*
      END
```

IPX source code development is assisted by the use of the *make* utility which is responsible for organizing compilation and loading of applications in the UNIX environment. Use of the *make* command is very straightforward. Simply go into the UNIX directory containing both the *Makefile* and the UNIX source and type *make* at the UNIX prompt. This will force compilation of any source files that have not already been compiled since they were last updated, and link the resulting object files into the application executable program; i.e., *ipx-2.7.4.x*.

The instructions for compiling and loading or *linking* the application are contained in a file named *Makefile* and are unfortunately complex. Most alterations to this file should be made by the developers, however, some simple modifications to the *make* procedure of IPX are possible. Changing the compilation flags is accomplished by editing *Makefile*, locating the string *FFLAGS*, and changing its arguments as desired. Similarly, new subprograms can be added to the application by placing their source and object file names in the respective *SOURCE* and *OBJECTS* macro lists of *Makefiles*.

5.4 IPX PROGRAM DESCRIPTION

Figure 5.1 is a flowchart of IPX and illustrates the functional relationships among the subroutines. IPX is a modular program. Its many subroutines can be grouped into the functional categories of input, process, output, and utility. The main program calls input subroutines, calls subroutine EULER, and closes files at the end of the simulation. The input subroutines are called

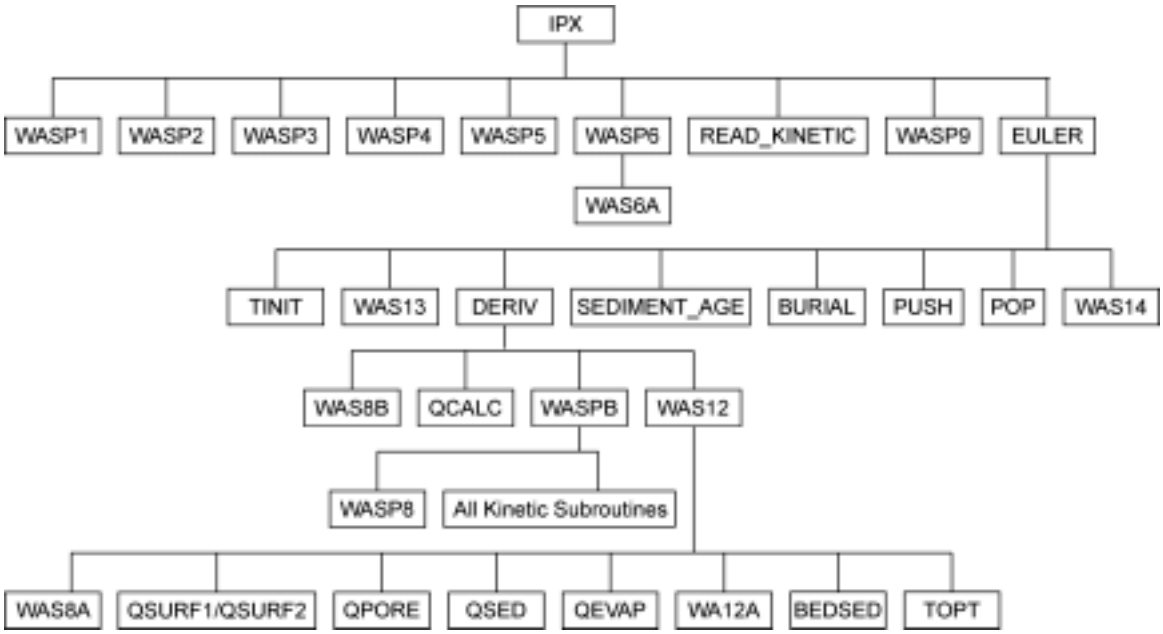


Figure 5.1. Hierarchy of major subprogram units in IPX.

sequentially, as shown. Subroutine EULER controls the actual simulation and calls DERIV each time-step to recalculate mass derivatives. The output subroutines are called sequentially as shown after the simulation is completed. Utility subroutines are called by the other subroutines as needed. Data are shared among the subroutines primarily through common blocks.

5.4.1 Main Program

IPX_R1:

The IPX_R1 main program is the control module. It operates the calling sequence for the input, calls subroutine EULER, and closes files at the end of the simulation.

5.4.2 Input Subroutines

WASP1

WASP1 opens the input and output units, then reads Data Group A for model identification and system bypass options. Information is printed and values and arrays are initialized. The subroutine then returns control to the main program.

WASP2

WASP2 reads Data Group B for sets of dispersion coefficients, cross-sectional areas, and characteristic lengths. These are converted to bulk exchanges, and information is stored in memory and printed. The subroutine then returns control to the main program.

WASP3

WASP3 reads Data Group C for volumes. If indicated, volumes are read from the *.RST restart file. Information is stored in memory and printed. The subroutine then returns control to the main program.

WASP4

WASP4 reads Data Group D for advective flows, which are converted to internal units of cubic meters per day. Information is stored in memory and printed. The subroutine then returns control to the main program.

WASP5

WASP5 reads Data Group E for boundary concentrations for each model system. Information is stored in memory and printed. The subroutine then returns control to the main program.

WASP6

WASP6 reads Data Group F for waste loads for each model system. Information is stored in memory and printed. If indicated, WASP6 calls subroutine WAS6A to read non-point source loads from an external file. The subroutine then returns control to the main program.

WAS6A

WAS6A opens an unformatted non-point source loading file NPS.DAT. The structure of the NPS.DAT file is presented in Table 5.1. The runoff day corresponding with the initial IPX simulation day is read. Input segment numbers corresponding to each runoff load are read. Actual runoff loads from the file are printed as specified. Finally, the file pointer is positioned properly to begin the simulation. The subroutine then returns control to subroutine WASP6.

READ_KINETIC

READ_KINETIC reads Data Group G for parameters for each segment. It then reads Data Group H for chemical constants. Finally, it reads Data Group I for kinetic time functions.

Table 5.1. Structure of the non-point source load file *NPS.DAT*.

Record Number		Contents of Record
1		NWKS
2		((NPSWK(I,J), I=1,NOSYS), J=1,NWKS)
3		((NPSWK(I,J), I=1,NOSYS), J=1,NWKS)
.		.
.		.
.		.
N + 1		((NPSWK(I,J), I=1,NOSYS), J=1,NWKS)
Variable	Type	Definition
NWKS	I*4	The number of runoff loads
NPSWK	R*4	Runoff loads averaged over day, kg/day
NOSYS	I*4	Number of water quality variables (or systems)
I	I*4	Water quality variable counter
J	I*4	Runoff load counter
N	I*4	Number of days for which loads are available

Information is stored in memory and printed. The subroutine then returns control to the main program.

WASP9

WASP9 reads Data Group J for bulk densities, maximum concentration, initial concentrations, and dissolved fractions in all segments for each model system. If indicated, initial concentrations are read from the *.RST restart file. Information is stored in memory and printed. Then WASP9 reads Data Group K for surficial sediment age layer characteristics. This information is also stored in memory and printed. The subroutine then returns control to the main program.

5.4.3 Output Subroutines

AVERAGING

AVERAGING is called by subroutine TOXIDU to perform time averaging of simulation results for output to the *.DMA file.

TOXIDU

TOXIDU is called by subroutine WASPB at specified intervals to write simulation output to the *.DMP and *.DMA files.

WRITEEXPDATA

WRITEEXPDATA is called in WAS13 at specified intervals to write export results to the *.EXP file.

WRITEMSBDATA

WRITEMSBDATA is called in EULER at the end of a simulation to write mass balance results to the *.MSB file.

WRITERSTDATA

WRITERSTDATA is called in EULER at specified intervals to write simulation restart information to the *.RST file.

5.4.4 Simulation Control and Process Subroutines to Compute

EULER

EULER is the computational engine of IPX. EULER performs the first-order numerical integration of the mass balance equations. First, counters and time functions are initialized to TZERO as needed by subroutine TINIT. Subroutine WAS13 is called to set up initial printouts. Subroutine DERIV is called to compute initial mass derivatives. Input data are initially screened for fatal error conditions and then the integration (simulation) proceeds, time-step by time-step.

For each time-step, EULER loops through each system and segment, calls subroutines DERIV, SEDIMENT_AGE, and BURIAL, and computes the new mass as follows:

new mass = old mass + mass derivative x time-step

Each new concentration is set to the new mass divided by the new volume, and the mass derivative is reset to zero. Unless the negative solution option is active, any negative concentrations are replaced by one-half of the old mass divided by the new volume. Next, EULER increments the time and adjusts the new day counter if necessary. When intermediate print times are reached, EULER calls subroutine WAS13 to produce intermediate printouts and triggers storage of all display variables (by returning IDISK = 1). Volumes are stored if IDISK = 1. The final task for each time-step is to check for a new time-step and for the end of the simulation. Subroutine WAS14 is called if it is time to use a new time-step.

When the final time for the simulation is reached, EULER triggers a final storage of display variables, then stores final volumes and concentrations in the *.RST file. At the end of the simulation, the subroutine returns control to the main program.

DERIV

DERIV is called by EULER to calculate mass derivatives. Subroutines WAS8B and QCALC is called to update flow and exchange time functions. Subroutine WASPB is called to obtain kinetic derivatives. Subroutine WAS12 is called to obtain transport and loading derivatives.

WASPB

WASPB is the subroutine that controls the computation of kinetic mass derivatives. WASPB calls subroutine WASP8 and all other subroutines necessary to compute the kinetic portion of the mass derivative. An overview subroutine WASPB and all kinetic subroutines is presented in Section 5.3.5.

WAS12

WAS12 is called by DERIV to obtain the transport and loading derivatives. Upon entry to WAS12, only the kinetic portion of the mass balance derivative has been evaluated by WASPB. WAS12 calls subroutines WA12A, WAS8A, and BEDSED to determine the proper upstream and downstream concentrations for advective flow and dispersive exchange and to update time functions and sediment conditions. Then WAS12 calls subroutines QSURF1 or QSURF2, QPORE, QSED, and QEVAP and calculates the mass derivatives due to advective flow, dispersive exchange, point source waste loading, and runoff loading, and adds them to the kinetic derivative. WAS12 goes through the following steps:

a. Using the IQ and JQ vectors as drivers, WAS12 computes advective transport. For each system, variable boundary concentrations are updated by calling WAS8A if necessary. For each flow, Q, proper upstream and downstream concentrations are assigned by calling WA12A. The advected concentration CSTAR is determined, and mass derivatives for the downstream and upstream segments are adjusted by ± Q CSTAR.

b. Using the IR and JR vectors as drivers, WAS12 computes dispersive transport. For each system and each exchange flow, R, proper upstream and downstream

concentrations C_2 and C_1 are assigned by calling WA12A. Mass derivatives for the downstream and upstream segments are adjusted by ± R (C_2-C_1).

c. Using the IWK vector as a driver, WAS12 computes point source loading. For each system, variable loadings are updated by calling WAS8A if necessary. For each load L (in kg/day), the mass derivative for the affected segment is adjusted by + L.

d. Using the INPS vector as a driver, WAS12 computes diffuse source loading if appropriate. New loads are read from file NPS.DAT at the beginning of each new day. For each load L' (in kg/day), the mass derivative for the affected segment is adjusted by + L'.

WA12A

WA12A is called by WAS12 to determine the proper upstream and downstream concentrations C_2 and C_1 for advective flow from segment JQ to segment IQ or dispersive exchange between segments JR and IR. For flows or exchanges with a downstream boundary, the proper boundary concentration is located for C_1. For flows or exchanges with an upstream boundary, the proper boundary concentration is located for C_2.

WASP8

WASP8 is called by subroutine WASPB and updates piecewise linear time functions, if any, for kinetic time functions. This means computing new slopes and intercepts, and setting a variable to indicate the next simulation time that the functions are to be updated. The following convention is used for the i^{th} update:

$$\text{slope} = \frac{f(t)_{i+1} - f(t)_i}{t_{i+1} - t_i}$$

$$\text{intercept} = f(t)_{i+1}$$

$$\text{next update time} = t_{i+1}$$

WAS8A

WAS8A updates piecewise linear time functions, if any, for boundary conditions and forcing functions. This means computing new slopes and intercepts for any system or state variable that requires an update, and setting a variable to indicate the next simulation time that

the piecewise linear functions are to be updated. The same conventions used in WASP8 are used in WAS8A for computing slopes and intercepts.

WAS8B

WAS8B updates piecewise linear time functions for dispersion coefficients and flows. Updated dispersion coefficients for each exchange field and time function are stored in the array BRINT(NF,NT). Updated flows for each field and time function are stored in the array QINT(NF,NT).

QCALC

QCALC, called in DERIV, sums the flows from all time functions for each segment.

QSURF1/QSURF2

QSURF1 or QSURF2, called in WAS12, compute the mass derivative due to surface water (advective) flow. QSURF1 is called only if IQOPT = 1. QSURF2 is called only if IQOPT = 2. Surface water flow options (IQOPT) are described in Section 1.4.1.

QPORE

QPORE, called in WAS12, computes the mass derivative due to pore water flow.

QSED

QSED, called in WAS12, computes the mass derivative due to settling and resuspension.

QEVAP

QEVAP, called in WAS12, computes the mass derivative due to precipitation and evaporation.

BEDSED

BEDSED, called in WAS12, computes changes in volumes and porosities for sediment bed segments, depending upon the sediment bed option used. For surficial sediment bed segments, porosity is constant but volumes change in response to net difference between the settling and resuspension fluxes. When the sedimentation (compaction) time interval is reached, mass is transported between surficial and subsurface sediment segments. The porosity and volume of all subsurface sediment segments are constant.

SEDIMENT_AGE

SEDIMENT_AGE, called in EULER, manages the aging process for solids and associated chemicals in each age layer of the surficial sediments.

BURIAL

BURIAL, called in EULER, computes the mass derivative due to upward (scour) and downward (burial) movement of solids and associated chemicals through the surficial and subsurface sediments for the Eulerian sediment bed option.

PUSH

PUSH, called in EULER, performs ghost collapse as specified by the ghost collapse option and computes the downward re-indexing of sediment segments and ghost stack elements for the semi-Lagrangian sediment bed option.

POP

POP, called in EULER, computes the upward re-indexing of sediment segments and ghost stack elements for the semi-Lagrangian sediment bed option.

WAS13

WAS13 is called every print interval by EULER to print intermediate concentrations or mass checks on a designated constituent. At this time, the solution stability is checked by comparing the maximum concentrations specified by the user with calculated concentrations. If any concentrations exceed the maximum, the simulation is stopped (aborted).

WAS14

WAS14 is called by EULER to adjust the integration step size (time-step) as specified by the user in Data Group A.

TINIT

TINIT is called by EULER at the beginning of the simulation to adjust time functions to the initial time TZERO. TINIT checks and adjusts time functions for exchanges, flows, kinetic time functions, boundary concentrations, and loads.

AVEINIT

AVEINIT is called by TOXIDU to initialize program variables used to perform time averaging of simulation results.

TOPT

TOPT can be called by the user WASPB subroutine to maximize the time-step subject to the flow and dispersion stability constraints. This should reduce numerical dispersion, but is not unconditionally stable. The time-step is calculated by TOPT every 0.5 days will fall between 0.01 and 0.5 days. **Note: the operation of subroutine TOPT has not been verified. The authors recommend that users input the time-step in Data Group A.**

5.4.5 Utility Subroutines

BRKERR

BRKERR prints an error message to output file and screen concerning the number of data points in a time function; the simulation is aborted.

FMTER

FMTER prints an error message to output file and screen concerning input data formats; the simulation is aborted.

GETMES

GETMES retrieves text messages from the messfile_r1.dat file for subsequent output to screen.

PRTSCR

PRTSCR prints text messages to screen.

SETCA

SETCA sets a character array to a specified character value.

SETIA

SETIA sets an integer array to a specified integer value.

SETRA

SETRA sets a real array to a specified real value.

SETRB

SETRB sets a real three-dimensional array to a specified real value.

SETXA

SETXA sets a double precision array to a specified double precision value.

TSTAMP

TSTAMP write a time and date at the state of a simulation to the *.OUT, *.DMP, *.EXP, and *.DMA files.

WERR

WERR writes error messages for improper segment designations and missing boundary conditions; the simulation is aborted.

WEXIT

WEXIT aborts the simulation when error conditions are encountered.

WMESS

WMESS prints a message when stability criteria are violated; the simulation is aborted.

5.4.6 Toxic Chemical Kinetic Subroutines

Source code for IPX toxic chemical kinetics are written in a modular structure that includes numerous subroutines as presented in Figure 5.2. Each transformation and transfer process is separated into one or several subroutines. This structure allows for convenient addition or modification of the kinetic descriptions.

WASPB

WASPB is the central water quality subroutine that calculates the kinetic mass derivative and stores the proper display variables for later printout. WASPB calls other subroutines as presented in Figure 5.2. WASPB is called every time-step by subroutine EULER and performs the following tasks:

1. At the start of a simulation, subroutine TOXINT is called to initialize parameters for kinetic processes. Chemical diffusivities at 25°C, basic partitioning parameters, and transformation rates and are initialized.

2. The current values for the piecewise-linear time functions of time are calculated. WASP8 is called if a time-break has been reached for any of the functions.

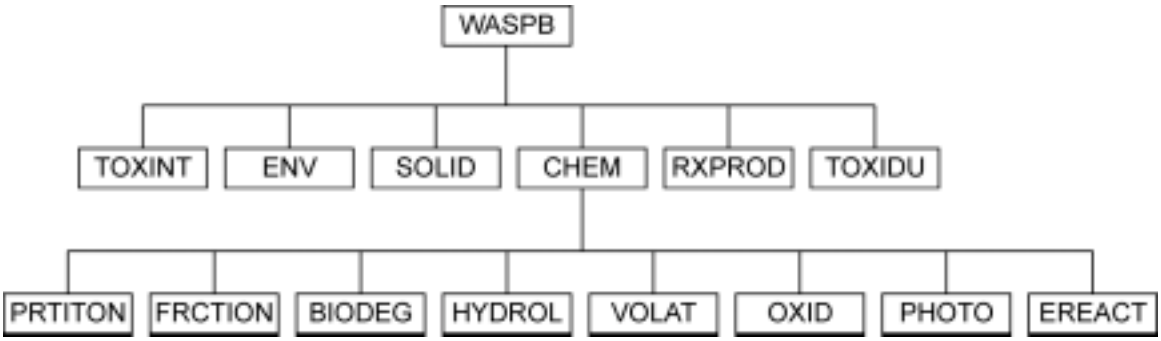


Figure 5.2. Hierarchy of major kinetic process subroutines in IPX.

3. For each segment of the model the following tasks are performed:

   a. Subroutine ENV is called to evaluate current environmental characteristics.

   b. Subroutine CHEM is called to evaluate the kinetic portion of the derivative describing a chemical. Effective rate constants for kinetic processes are stored in memory.

   c. Subroutine SOLID is called to evaluate the kinetic derivative for each solid type. (There are no kinetic for solids in the present code.) Locations in the F array that the transport of solids in the transport fields are set.

   d. If a print interval has been reached, subroutine TOXIDU is called to store simulation results in the *.DMP and *.DMA files.

CHEM(I)

CHEM determines the kinetic portion of the derivative describing a chemical in segment I. Tasks executed are:

1. Subroutine PRTION is called to determine the partition coefficient of the chemical.

2. The Henry's Law constant and air-water partition coefficient for the chemical are computed.

3. Subroutine FRCTION is called to determine the fraction of total chemical in each of the 3 phases (dissolved, DOC-bound, and sorbed to solids).

4. Subroutines BIODEG, HYDROL, PHOTO, VOLAT, OXID and EREACT are called to determine the transfer and transformation rates that make up the kinetic portion of the derivative.

5. The individual rates returned by the subroutines called are summed to yield the total kinetic portion of the derivative.

6. The derivative is multiplied by the segment volume to be consistent with the transport derivative calculation.

ENV

ENV computes segment-specific physical and chemical characteristics of each segment.

PRTITON(ICHEM)

PRTITON computes the equilibrium partition coefficients defining sorption of chemical ICHEM to each of the three solids types in segment I. For the neutral chemical, the classical partition coefficient (PIXC) is computed from the organic carbon partition coefficient and the fraction organic carbon of the solids. The partition coefficients (PART) are calculated from PIXC using the particle interaction model for sorption (see Section 1.5).

FRCTION(ICHEM, DISTRIB, PIDOC)

FRCTION computes the fraction of chemical ICHEM in segment I present in the dissolved, DOC-bound and particulate (solids-sorbed) phases. This computation consists of 3 parts:

1. Distribution factors are computed for each phase. A distribution factor is the ratio of component concentration to dissolved neutral chemical concentration. It is calculated for sorbed chemical. The distribution factors for dissolved ionic chemical are passed to FRCTION as subroutine argument DISTRIB.

2. The distribution factors are summed. As part of the summation the factor for dissolved components are multiplied by the porosity of the segment (PORE).

3. The fractions are computed as the distribution factor divided by the sum of distribution factors.

4. Chemical concentrations in each phase are computed from the total concentration and the distribution coefficient.

5. Locations in the F array that define the transport of the chemical in the transport fields are set.

BIODEG(ICHEM)

BIODEG computes the loss rate of chemical ICHM in segment I due to biodegradation. Separate loss rates are computed for solids sorbed chemical (BIOS) and dissolved and DOC-bound chemical (BIOW) using 20°C rates passed to the routine in array KBIO20 and temperature correction factors passed in arrays Q10DIS (dissolved chemical), Q10DOC (DOC-bound chemical) and Q10PAR (solids sorbed chemical).

HYDROL(ICHEM)

HYDROL computes the loss rate of chemical ICHM in segment I due to chemical hydrolysis. Separate loss rates (μg/L-d) are computed for alkaline hydrolysis (ALKH), neutral hydrolysis (NEUTH) and acid hydrolysis (ACIDH) using 20°C rates passed to the routine in array KH20 and Arrhenius temperature correction factors passed in arrays EHOH (alkaline hydrolysis), EHN (neutral hydrolysis) and EHH (acid hydrolysis).

PHOTO(ICHEM)

PHOTO computes the loss rate of chemical ICHEM in segment I due to photolysis. If the user has selected photolysis option 1 (IPHOTO = 1), the specified depth-integrated photolysis rate constant (KDPG) and quantum yield (QUANTG) for each photolyzing phase are used to compute as the overall photolysis loss as the product of the rate constant, the quantum yield, and chemical concentration in each phase.

VOLAT(ICHEM, VLT)

VOLAT computes the rate of loss by volatilization of a chemical ICHEM in segment I. The calculation approach used depends on the volatilization options (XVL and XVG) selected by the user.

OXID(ICHEM)

OXID computes the loss rate of chemical ICHM in segment I due to chemical oxidation. Separate oxidation rates are computed for dissolved, DOC sorbed and solids sorbed chemical fraction using 20°C rates passed to the routine in array KOX20 and Arrhenius temperature correction factors passed in array EOX. These rates are summed and an overall oxidation rate is computed.

EREACT(ICHEM)

EREACT computes the loss rate of chemical ICHEM in segment I due to the user-defined extra reaction.

SOLID

SOLID computes transport fractions and kinetic derivatives for solids state variables.

TOXINT

TOXINT is called by WASPB at the start of a simulation to initialize parameters for kinetic processes. Chemical diffusivities in water and air at 25°C, basic partitioning parameters, and transformation rates and are initialized. This subroutine is only called one time, at the start of a simulation.

5.5 INPUT AND OUTPUT UNITS

All the input/output (I/O) units can be reassigned an integer value in the WASP MAIN subroutine. However, new users should first develop a firm understanding of the structure and function of the program before reassigning I/O units. A brief description of each I/O-related integer and its default value follows:

AUX: Default value is 4. AUX refers to the use of an auxiliary flow file. This file has been created outside the WASP programs and is used to input flows and volumes. Example: READ(AUX).

IN: Default value is 2. The value 2 refers to the input data set. Input data set is a sequential formatted file. May also be used to represent the integer 2. Example: READ(IN).

OUT: Default value is 5. OUT refers to the output file *.OUT, a sequential formatted file. Example: WRITE(OUT).

RESRT: Default value is 9. RESTRT refers to the *.RST file that contains a snapshot of model conditions which can be used as initial conditions for a sequence of simulations or restoring a simulation that did not complete. Example: WRITE(RESTRT).

MESS: Default value is 6. MESS is used to write inquiry messages to the screen and display run time status messages. For more information see MFLAG variable in Data Group A.

IEXP: Default value is 16. IEXP is used to write the mass exported across a model interface during the simulation to the *.EXP file for any one state variable and total solids as specified in the input data file.

IMASS: Default value is 20. IMASS is used to write the mass balance file for all systems.

IDMP: Default value is 15. IDMP is used to write all instantaneous (point-in-time) simulation results that can be latter recalled and printed out using the W4DIS274 post-processing program.

IDMA: Default value is 25. IDMA is used to write all time averaged simulation results that can be latter recalled and printed out using the W4DIS274 post-processing program.

5.6 COMMON BLOCKS

Common blocks permit program subroutines to share data. The common blocks also contain the parameter statement assignments used to control the dimension of variables that constrain the maximum possible size of a simulation. The user can change the maximum dimension of a simulation by changing the values assigned to each parameter, compiling, and linking the source code. A brief description of each common block follows:

AVERAGE.CMN: Common block used by output subroutines to compute time averaged results from simulation calculations.

CONC.CMN: Common block used by kinetic process subroutines to store chemical concentrations from simulation calculations.

ENVIRON.CMN: Common block used by kinetic process subroutines to store environmental information.

IPX.CMN: Common block used to declare general variables used throughout the code. This common block also contains the PARAMETER statements that control the dimension of simulation constraint parameters, such as number of segments and number of systems.

KNETIC.CMN: Common block used by kinetic process subroutines to store degradation rates and constants.

PARAM.CMN: Common block used by kinetic process subroutines to store information related to the environmental parameters and time functions.

PHYSCHM.CMN: Common block used by the kinetic process subroutines to store information related to the physical-chemical calculations.

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APPENDIX A

IMPLEMENTATION OF THE MASS BALANCE EQUATION

IPX solves a finite difference approximation of Equation 1.1 for a model network that represents the important characteristics of the real water body. This section explains the derivation of the finite difference mass balance equation using the one-dimensional form for convenience. Regrouping the terms in Equation 1.2 for mathematical convenience gives:

$$\frac{\partial}{\partial t}(AC) = \frac{\partial}{\partial x}(QC) + \frac{\partial}{\partial x}\left(E_x A \frac{\partial C}{\partial x}\right) + AS^T \qquad \text{(A.1)}$$

where: S^T = total source/sink rate = $S_L + S_B + S_K$, g/m^3-day
Q = volumetric flow = A U_X, m^3/day

Assuming that derivatives of C are single-valued, finite, continuous functions of x, as in Figure A1, then the Taylor's series expansion gives:

$$C_{x_0+\Delta x} = C_{x_0} + \Delta x \left.\frac{\partial C}{\partial x}\right|_{x_0} + \Delta x^2 \left.\frac{\partial^2 C}{\partial x^2}\right|_{x_0} + \frac{1}{2}\Delta x^3 \left.\frac{\partial^3 C}{\partial x^3}\right|_{x_0} + \cdots \qquad \text{(A.2)}$$

$$C_{x_0-\Delta x} = C_{x_0} - \Delta x \left.\frac{\partial C}{\partial x}\right|_{x_0} + \Delta x^2 \left.\frac{\partial^2 C}{\partial x^2}\right|_{x_0} - \frac{1}{2}\Delta x^3 \left.\frac{\partial^3 C}{\partial x^3}\right|_{x_0} + \cdots \qquad \text{(A.3)}$$

Assuming that terms containing third and higher order powers of Δx are negligible in comparison with the lower powers of Δx, Equations A.2 and A.3 can be subtracted to give:

$$\left.\frac{\partial C}{\partial x}\right|_{x_0} = \frac{C_{x_0+\Delta x} - C_{x_0-\Delta x}}{2\Delta x} + Error\ term \qquad \text{(A.4)}$$

The error term is of order Δx^2. Referring to Figure A1, Equation A.4 states that the slope of the line AB is equal to the slope of the tangent centered at P. This is known as the central-difference

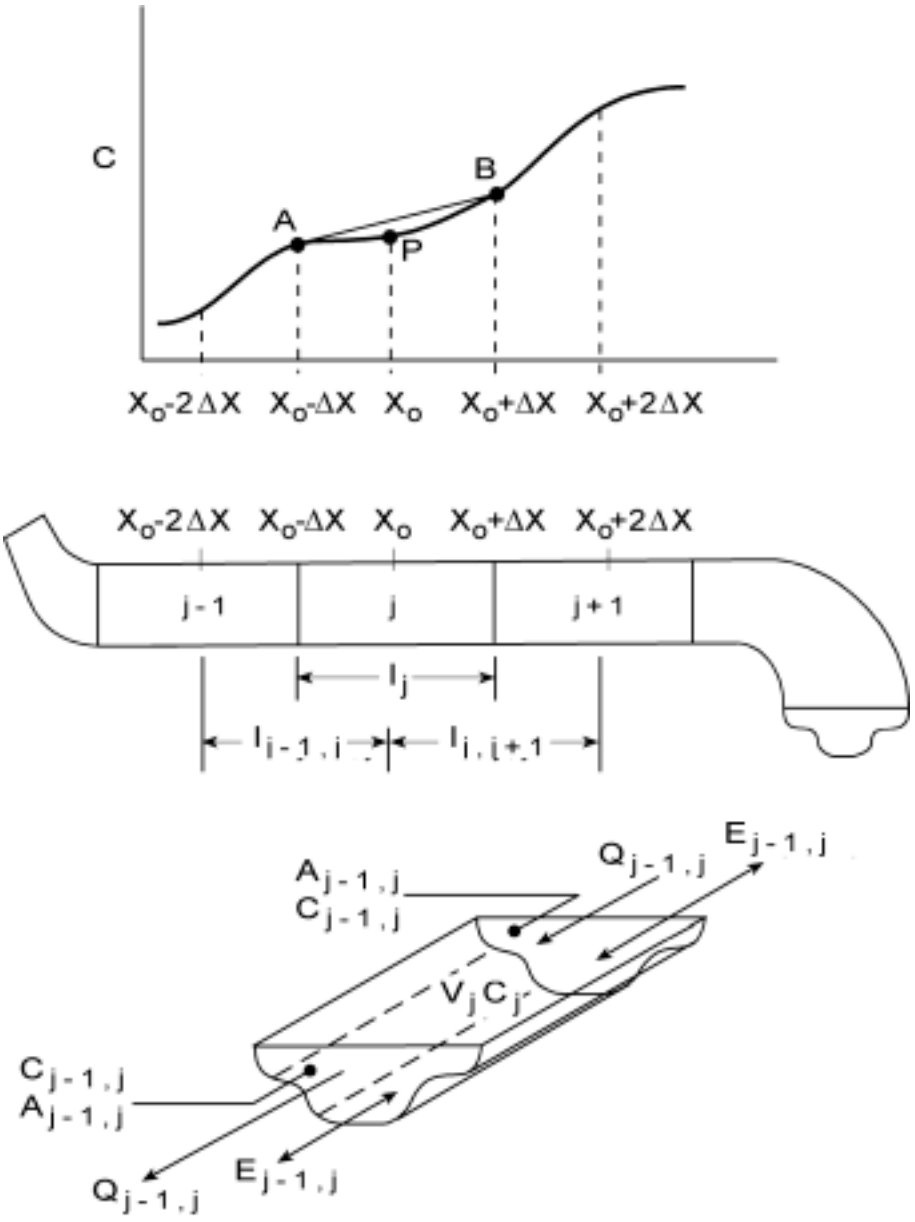

Figure A1. Definition sketch for finite difference equation.

approximation. The slope at P may also be approximated by the slope of the line PB, giving the forward-difference formula:

$$\left.\frac{\partial C}{\partial x}\right|_{x_0} = \frac{C_{x_0+\Delta x} - C_{x_0}}{\Delta x} \tag{A.5}$$

Similarly, the slope at P may be approximated by the slope of the line AP, giving the backward-difference formula:

$$\left.\frac{\partial C}{\partial x}\right|_{x_0} = \frac{C_{x_0} - C_{x_0+\Delta x}}{\Delta x} \tag{A.6}$$

Equations A.4 and A.6 can be obtained from A.2 and A.4, respectively, by assuming that the second and higher order powers of Δx are negligible. The error term for both the forward and backward difference approximations is of order Δx.

Substituting the central difference approximation into the advection term of Equation A.1 gives:

$$\frac{\partial}{\partial x}(QC) = \frac{Q_{x_0+\Delta x} C_{x_0+\Delta x} - Q_{x_0-\Delta x} C_{x_0-\Delta x}}{2\Delta x} \tag{A.7}$$

Similarly, the dispersion term becomes:

$$\frac{\partial}{\partial x}\left(E_x A \frac{\partial C}{\partial x}\right) = \frac{\left(E_x A\right)_{x_0+\Delta x} \left.\frac{\partial C}{\partial x}\right|_{x_0+\Delta x} - \left(E_x A\right)_{x_0-\Delta x} \left.\frac{\partial C}{\partial x}\right|_{x_0-\Delta x}}{2\Delta x} \tag{A.8}$$

Substituting the central difference approximation for $\left.\frac{\partial C}{\partial x}\right|_{x_0 \pm \Delta x}$ in Equation A.8 gives:

$$\begin{aligned}\frac{\partial}{\partial x}\left(E_x A \frac{\partial C}{\partial x}\right) = & \frac{\left(E_x A\right)_{x_0+\Delta x} \Delta x \dfrac{C_{x_0+2\Delta x} - C_{x_0}}{2\Delta x}}{2\Delta x} \\ & - \frac{\left(E_x A\right)_{x_0-\Delta x} \Delta x \dfrac{C_{x_0} - C_{x_0-2\Delta x}}{2\Delta x}}{2\Delta x}\end{aligned} \tag{A.9}$$

When applying the difference approximations to segment j of a network as in Figure A1, x_o corresponds to the center of j, $x_0 + \Delta x$ to the interface between j and j+1, $x_0 - \Delta x$ to the interface between j-1 and j, $x_0 + 2\Delta x$ to the center of j+1, and $x_0 - 2\Delta x$ to the center of j-1. The mass balance equation for segment j can be written:

$$\frac{\partial}{\partial t}\left(A_j C_j\right) = -\frac{Q_{j,j+1}}{L_j} C_{j,j+1} + \frac{Q_{j-1,j}}{L_j} C_{j-1,j} + \frac{\left(E_X A\right)_{j,j+1}}{L_j L_{j,j+1}}\left(C_{j+1} - C_j\right) - \frac{\left(E_X A\right)_{j-1,j}}{L_j L_{j-1,j}}\left(C_j - C_{j-1}\right) + A_j S_j^T \qquad \text{(A.10)}$$

Multiplying through by Lj gives:

$$\frac{\partial}{\partial t}\left(V_j C_j\right) = -Q_{j,j+1} C_{j,j+1} + Q_{j-1,j} C_{j-1,j} + R_{j,j+1}\left(C_{j+1} - C_j\right) - R_{j-1,j}\left(C_j - C_{j-1}\right) + V_j S_j^T \qquad \text{(A.11)}$$

where: V_j = volume of segment j = A_j Lj, m^3
R = dispersive flow = E A/L_c, m^3/day
L_c = characteristic length, m

The interfacial concentrations $C_{j,j+1}$ and $C_{j-1,j}$ must be expressed in terms of the segment concentrations:

$$C_{j,j+1} = \omega C_{j+1} + (1-\omega) C_{j-1} \qquad \text{(A.12)}$$

$$C_{j-1,j} = \omega C_j + (1-\omega) C_{j-1} \qquad \text{(A.13)}$$

where: ω = numerical weighting factor (advection factor) between 0 and 1

Specifying ω = 0 gives a backward difference approximation for the advective term, ω = 0.5 gives a central difference approximation, and ω = 1 a forward difference

Equation A.11 can be extended to the multi-dimensional form used in IPX. Consider i segments adjoining segment j. Interfaces are denoted ij. The general equation becomes:

$$\frac{\partial}{\partial t}\left(V_j C_j\right) = -\sum_i Q_{ij} C_{ij} + \sum_i R_{ij}\left(C_i - C_j\right) + \sum_L V_j S_{Lj} + \sum_B V_j S_{Bj} + \sum_K V_j S_{Kj} \quad \text{(A.14)}$$

where: Q_{ij} = flow, defined as positive when leaving segment j, and negative when entering j, m^3/day

Equation A.14 is the general expression used in IPX to evaluate the mass derivatives for every segment j during each time-step t between the initial time t_0 and the final time t_F. Given concentrations and volumes at time t, IPX calculates new masses at $t + \Delta t$ using the one-step Euler scheme:

$$\left(V_j C_j\right)_{j,t+\Delta t} = \left(V_j C_j\right)_t + \frac{\partial}{\partial t}\left(V_j C_j\right)_t \Delta t \quad \text{(A.15)}$$

where: Δt = time-step (typical values between 0.001 and 0.5 days), days

Given new masses at time $t + \Delta t$, IPX computes the new concentrations by dividing the new masses by the new volumes:

$$C_{j,t+\Delta t} = \frac{\left(V_j C_j\right)_{j,t+\Delta t}}{V_{j,t+\Delta t}} \quad \text{(A.16)}$$

The new volumes are calculated internally from the specified (or computed) flow fields using the principle of continuity.

During normal simulations, IPX prohibits segment concentrations from going negative and causing numerical instability of the solution. A negative concentration might be calculated for constituents with low concentrations in the vicinity of significant spatial gradients. If a calculated mass derivative would drive a segment concentration below zero at $t + \Delta t$, IPX maintains a positive segment concentration by halving the mass that is present at time t. Experience shows that this procedure is generally acceptable. Users can activate or disable this negative solution procedure through the use of negative solution option in Data Group A. If negative concentrations and instability occur when this option is disabled, the simulation can be repeated with a smaller time-step.